June 1975 4 Report No. Env. E. 52-75-6

Evaluation of Process Design Parameters For Phosphorus Removal From Domestic Wastewaters By Chemical Clarification

Stuart P. Bowen Francis A. DiGiano

Report to the Division of Water Pollution Control Massachusetts Water Resources Commission Contract Number 73-07-(01)



ENVIRONMENTAL ENGINEERING DEPARTMENT OF CIVIL ENGINEERING UNIVERSITY OF MASSACHUSETTS AMHERST, MASSACHUSETTS

EVALUATION OF PROCESS DESIGN PARAMETERS FOR PHOSPHORUS REMOVAL FROM DOMESTIC WASTEWATERS BY CHEMICAL CLARIFICATION

Вy

Stuart P. Bowen Research Assistant

Francis A. DiGiano Associate Professor of Civil Engineering

Division of Water Pollution Control Massachusetts Water Resources Commission Contract Number MDWPC 73-07(1)

Environmental Engineering Program Department of Civil Engineering University of Massachusetts Amherst, Massachusetts 01002

June 1975

ABSTRACT

Although generally successful, biological wastewater treatment processes are very costly, have limited efficiency, are susceptible to upset, and possess a limited ability to remove algal nutrients. Chemical, rather than biological, processes can overcome many of these problems, but little guidance is available in the literature for the engineer to design these systems.

Raw wastewater was treated with alum or lime in jar test flocculation experiments to determine the optimum chemical doses and pH values to remove phosphorus, suspended solids, turbidity, and total organic carbon. Flocculation and sedimentation effects were studied in a column in which the mixing intensity could be controlled and measured.

Alum and lime produced comparable results, but effects due to alum pH-dose interactions allowed only a small region of optimum results indicating that careful pH control would be required. Lime coagulation was equally effective, and pH values would not need to be as precise. However, an unusually high pH was required with lime due to the low alkalinity of the local water supply.

It had been anticipated that the level of mixing intensity during flocculation would have a significant effect on process performance, but very little effect was observed provided that the mixing intensity was great enough to prevent deposition of solids. Design curves and testing methodologies were presented which will enable the engineer to select optimum coagulant dose, pH, flocculation intensity, and sedimentation time for chemically assisted clarification processes.

۰,

.

TABLE OF CONTENTS

ABSTRACT	i
TABLE OF CONTENTS	vi
LIST OF TABLES	vii
LIST OF ILLUSTRATIONS	ix
NOMENCLATURE	xii
INTRODUCTION	1
Problem Background	1
Historical Development	2
Research Scope	8
THEORETICAL CONSIDERATIONS	10
Status of Chemical Clarification Design	10
Procedures	12
Phosphorus Aquo-Chemistry	12
Wastewater Coagulation	16
Double-layer compression	20
Adsorption and charge neutralization	20
Enmeshment in a precipitate	22
Adsorption and interparticle bridging	23
Wastewater Flocculation	23
JAR TEST EXPERIMENTS	30
Purpose	30
Experimental Methods and Materials	30
Effects of pH and Alum Dose on Pollutant Removal	30

CONTENTS

,

	Page
Effects of pH and Lime Dose on Pollutant Removal	46
COLUMN EXPERIMENTS	58
Purpose	58
Experimental Equipment	58
Column Test Procedure	65
Column Test Results	72
Characterization of Lime and Alum Sludges	91
SUMMARY, CONCLUSIONS AND RECOMMENDATIONS	96
Summary	96
Conclusions	98
Recommendations	99
Future studies	99
Design recommendations	100
APPENDIX	101
BIBLIOGRAPHY	118

LIST OF TABLES

.

•

Table	Title	Page
1	Tertiary Treatment	4
2	Raw Sewage Treatment	6
3	Summary of Jar Test Procedures	33
4	Characteristics of Amherst Sewage	35
5	Summary of Jar Test Results	52
6	Jar Test Results Using Lime and Ferric Iron	55
7	Effect of Adding Settled Sludge to Lime Jar Tests	56
8	Settling Analysis of Coagulated Raw Sewage	67
9	Percent Removal of Suspended Solids at Varying Time	70
10	Settling Time vs. Percent Removal and Overflow Rate	70
11	Summary of Column Test Results	. 88
12	Sludge Volume in Column Tests	92
13	Sludge Dewatering Characteristics	94

viii

.

.

•

.

.

LIST OF ILLUSTRATIONS

Figure	Title	Page					
1	Equilibrium Solubility Diagrams for Aluminum and Calcium Phosphates	14					
2	Schematic Illustration of Electric Double Layer	19					
3	Schematic Illustration of Interaction Energy	19					
4	Effect of Sample Storage on Phosphorus and Carbon Determinations						
5	Percent Removal of Total Phosphorus Versus Alum Dose and pH	39					
6	Percent Removal of Suspended Solids Versus Alum Dose and pH	40					
7	Percent Removal of Turbidity Versus Alum Dose and pH	41					
8	Percent Removal of Total Organic Carbon Versus Alum Dose and pH	42					
9	Percent Removal of Total Phosphorus Versus Lime Dose and pH	47					
10	Percent Removal of Suspended Solids Versus Lime Dose and pH	48					
11	Percent Removal of Turbidity Versus Lime Dose and pH	49					
12	Percent Removal of Total Organic Carbon Versus Lime Dose and pH	50					
13	Flocculation/Sedimentation Column	59					
14	Column Flocculation Calibration Curve Relating Mixing Intensity to RPM	62					

LIST OF ILLUSTRATIONS (Continued)

ï

Figure	Title	Page
15	Schematic Diagram of Column Test System	64
16	Percent Removal of Suspended Solids Versus Column Depth and Sedimentation Time for Example Data	68
17	Overflow Rate Versus Percent Removal of Suspended Solids for Example Data	71
18	Percent Removal of Total Phosphorus Versus Overflow Rate for Alum Dose of 175 mg/l at pH 5.9	73
19	Percent Removal of Suspended Solids Versus Overflow Rate for Alum Dose of 175 mg/l at pH 5.9	74
20	Percent Removal of Turbidity Versus Overflow Rate for Alum Dose of 175 mg/l at pH 5.9	75
21	Percent Removal of Total Organic Carbon Versus Overflow Rate for Alum Dose of 175 mg/l at pH 5.9	76
22	Percent Removal of Total Phosphorus Versus Overflow Rate for Lime Dose of 300 mg/l.	77
23	Percent Removal of Total Phosphorus Versus Overflow Rate for Lime Dose for 400 mg/l	78
24	Percent Removal of Suspended Solids Versus Overflow Rate for Lime Dose of 300 mg/l	79
25	Percent Removal of Suspended Solids Versus Overflow Rate for Lime Dose of 400 mg/l	80
26	Percent Removal of Turbidity Versus Overflow Rate for Lime Dose of 300 mg/l.	81
27	Percent Removal of Turbidity Versus Overflow Rate for Lime Dose of 400 mg/1.	82

.

•

LIST OF ILLUSTRATIONS (Continued)

.

Figure	Title	Page
28	Percent Removal of Total Organic Carbon Versus Overflow Rate for Lime Dose of 400 mg/1	83
29	Percent Removal of Total Organic Carbon Versus Overflow Rate for Lime Dose of 400 mg/l	84
30	Column Mixing Speed Versus Sludge Volume	93

NOMENCLATURE

· ·

1--

ł

Symbol	Definition and Dimensions in Mass (M), Length (L), and						
	Time (T).						
А	Area (L ²)						
с _р	Drag Coefficient (dimensionless)						
$^{\rm F}{}_{ m D}$	Drag Force (ML/T^2)						
G	Root-Mean-Square Velocity Gradient (T^{-1})						
g	Gravitational Constant (L/T^2)						
k	Settling Velocity Ratio (dimensionless)						
р	Mixing Power (ML^2/T^3)						
r	Paddle Arm Length (L)						
S	Rotational Velocity (T ⁻¹)						
Т	Torque $(L^2 M/T^2)$						
v	Volume (L ³)						
v	Velocity (L/T)						
a	Velocity (L/T)						
μ	Absolute Viscosity (M/LT)						
ρ	Density (M/L^3)						
ω	Angular Velocity (T ⁻¹)						

.

.

CHAPTER I

1

INTRODUCTION

Problem Background

The purpose of wastewater treatment is to remove pollutants from wastewaters so that discharge of the treated effluent will not degrade the receiving body of water. Traditionally the pollutants of greatest concern have been those exerting an oxygen demand and the method of removal has been the biological treatment process. Although biological treatment processes have in the past generally been considered successful, their weaknesses are apparent: high cost, limited efficiency, susceptability to upset, and limited ability to remove the algal nutrients nitrogen and phosphorus (1, 2). As society demands greater environmental protection and becomes increasingly aware of the enormous cost of waste treatment, the future seems assured for a chemical waste treatment process which has the promise of easy control, high efficiency, and relative economy.

Among the chemical processes which can be applied to the treatment of wastewaters is coagulation using either inorganic minerals or long chain organic polymers. Application of coagulants to the treatment of sewage is not limited to new installations, but may be used to upgrade existing primary treatment processes and biological secondary treatment plants. As an aid to primary treatment, proper application of coagulants may achieve an effluent quality approaching that of secondary treatment and remove significant quantities of phosphorus. Existing biological treatment processes may be upgraded by use of coagulants to remove phosphorus and to improve removal of oxygen-demanding materials and suspended solids.

Historical Development

In 1944 Sawyer (3) called for the removal of fertilizing elements from sewage treatment plant effluents and reported results of studies on chemical treatment of sewages with ferric chloride to remove phosphorus. Rudolfs (4) demonstrated in 1947 that sewage phosphates are readily precipitated by lime. Owen (5) in 1953 found in jar tests that the phosphorus level of a trickling filter effluent could be reduced to about 0.25 mg/l by raising the pH to 10.75 with lime followed by settling for one hour.

Lea, et al. (6) reported in 1954 concerning studies at laboratory and pilot plant scale on phosphorus removal from sewage treatment plant effluents using ferrous sulfate, ferric sulfate, cupric sulfate, diatomaceous earth, and aluminum sulfate. He concluded that aluminum sulfate (alum) was the most effective coagulant because it yielded low residual phosphorus concentrations, about 0.07 mg/l or 99% removal. In jar tests he found that the optimum dose was 185 mg/l (as $Al_2(SO_4)_3 \cdot 14H_20$) and the optimum pH was in the range 7.1 to 7.7. When pH values either above or below this range were used alum coagulation was unsuccessful. Alum treatment also removed 87% of the BOD in the sewage treatment plant effluent and 62% of the total organic nitrogen. However, no ammonia, nitrate, or nitrite nitrogen was removed.

Additionally, these investigators studied the relation of flocculation time to phosphorus removal and found that the maximum removal occurred between 10 and 15 minutes.

In contrast to Lea's work, Malhotra et al. (7) in 1964, using filtered activated sludge sewage treatment plant effluent, concluded that lime was a more suitable chemical for phosphorus precipitation than alum based on performance and cost. They also concluded that when using alum the optimum pH was 5.75 ± 0.25 . The percentage removal of total phosphorus decreased as the initial phosphorus concentration in the sample increased. However, when using lime a dose of 450 mg/l as CaO at a pH of 11.0 removed 90 percent of the total phosphorus and the percent removal was independent of the initial phosphorus concentration. A major disadvantage of using lime was considered to be the high pH of the treated water.

When the above research showed that phosphorus removal could be accomplished fairly easily and inexpensively, and as the need for phosphorus removal from sewage became apparent (8) many other investigators worked with laboratory studies, pilot studies, and full scale treatment plants to demonstrate the effectiveness of lime, alum, and iron salts.

The results of these numerous investigations using lime and alum as coagulants to treat both raw sewage and sewage treatment plant effluents are incorporated in Tables 1 and 2. On the basis of these studies and other reports, the following general conclusions can be made:

 Lime and alum under proper dose and pH conditions achieve essentially the same removal efficiency at approximately the same cost (9, 12, 14, 15, 17, 18, 19, 20, 21).

TABLE 1--Tertiary Treatment

Chemical	Reference	Scale	Design Methods	OR gpd/ft ²	Alkalinity as CaCO3	Dose_mg/1	рН
Lime (CaO)	9	Pilot 0.1 MGD		1500 900 1060	100-150 100-150 100-150	340 290 +6-12 mg/1 Fe ³⁺ 260 +0.16 mg/1 anionic polymer	11.8 11.5 11.4
				1500	100-150	275	11.6
Lime	10	7.5 MGD	Jar Tests	395-600	226	300	10.9
Alum	6	Batch Pilot 10 gpm	Jar Tests Batch & Jar Tests			200 200	7.1-7.7 7.1-7.7
Alum Lime	7	Batch Batch				250 400 300	6.0 11.0 10.0
Alum Lime	1	Pilot 310 gpm	Jar Tests	950- 1035 655- 835 966		89* 130* 270 ^{**}	11.0
Lime	11	Pilot 100 gpm	<u>}</u>	720		128 +25 mg/1Fe ³⁺	
Lime	12	Pilot 75 gpm		1440			9.5

		P SS O ₂ Demand				O ₂ Demand		and			
Chemical	Init.	Final	% Rem.	Init.	Final	% Rem.	Init.	Final	Rem.	Remarks	
Lime (CaO)		1.0	87					19.5	45*	O ₂ Demand is TOC *two stage treatment	
		0.55 0.54 0.49	93 91 93					14.1 15.7 13.9	64 [*] 55 [*] 57	Single Stage	
Lime	8.4	1.3	85	22	37	+68	40.5	17.2	58	O ₂ Demand is COD	
Alum	5.9	0.8	86				 36	11.7	87 67.5	O ₂ Demand is BOD	
Alum			94						55	STP effluent filtered prior to flocculation O_2 Demand is COD	
Lime			90 10								
Alum	10.1 11.1	2.9 1.6	71 86	72 94	38 20	47 79	24 30	5 11	79 63	O ₂ Demand is BOD *Activated Silica at 9.5% of Alum.	
Lime	9.1	0.5	95	80	19	76	62	17	73	**Activated Silica at 2 mg/l	
Lime	6.5*	0.43*	93,5							*Soluble P	
Lime	1	< 1.0								Turbidity <0.5 JTU	

TABLE 1--Tertiary Treatment (Continued)

Chemical	Reference	Scale	Design Methods	OR gpd/ft ²	Alkalinity as CaCO3	Dose	рH
Lime (CaO)	13	Batch	Dose re- quired to raise pH to ll		100		11
	• • • • • • • • • • • • • • • • • • •	Batch			250		11
Lime	14	Batch	Dose re- quired to various pH values		222 222 222 222 222 222		8.5 9.5 10.3 11.0
Lime	15	Batch	Jar Tests		230	110	9.5
Lime	16	STP 1.5 MGD	Jar Tests		120	83	10.1
FeC13	17	Pilot 5 gpm	Jar Tests			170	6-7

TABLE 2 -- Raw Sewage Treatment

	P			SS			C ₂ Demand			· · · · · · · · · · · · · · · · · · ·
Chemical	Init.	Final	% Rem.	Init.	Final	% Rem.	Init.	Final	% Rem.	Remarks
Lime (CaO)	3.7	0.37 as P	90				100	44	56	O2 Demand is BOD
	11.5	2.0	84				237	69	71	
Lime	9.3 9.3	5.0 3.7	46 60				355 355	340 235	4 34	O ₂ Demand is COD P and O ₂ Demand on Settled Sewage
	9.3	2.2	76				355	210	41	"Tests" indicated OR = 2000 gpd/ft ²
	9.3	1.8	81			-	355	200	44	
Lime	13	1.6	88			90			60	O ₂ Demand is BOD
Lime			40			45			41	O ₂ Demand is COD Lime in Primary, then AS
FeCl ₃	9.8	0.8	92				50	15	70	Primary Effluent O ₂ Demand is BOD

TABLE 2 -- Raw Sewage Treatment (Continued)

2. The most likely applications for either lime or alum coagulation processes would be as an aid to primary treatment prior to a biological process (13, 15, 16, 17), as a tertiary treatment process to remove phosphorus and residual suspended solids from biological plant effluents (1, 7, 10, 22, 23, 24) or as a first step in a physicalchemical waste treatment process also utilizing activated carbon for removal of dissolved organics (9).

3. Lime precipitation is most efficient at pH values greater than 11. However, if the precipitation process is to be followed by a biological treatment process, a pH of about 9.5 is the maximum which can be tolerated without overtaxing the buffering capacity of the biological system (15, 16).

4. Regeneration of the coagulant is an economic necessity.
Recovery of CaO from lime precipitation sludge has been demonstrated (10, 25), and, although recovery of alum sludge is more difficult and is unproven in field scale tests, alum sludge can probably also be rei
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i
i

5. Methods of conducting tests for the design of chemically assisted waste treatment processes have not been standardized and many fundamental design criteria are not available in the literature.

Research Scope

The purpose of this research was to develop engineering data to allow the rational design of facilities to remove pollutants from raw domestic wastewater by chemical coagulation and sedimentation. The chemicals investigated were aluminum sulfate (alum) and calcium

oxide (lime) because these are the coagulants most common in sewage treatment and also represent two general classes of coagulants. Specifically, the purpose of this research was to determine the relationship between the effectiveness of chemical addition and important operational parameters; these parameters are coagulant dose, pH during coagulation, duration and intensity of flocculation, and duration of sedimentation.

Although chemical coagulation systems are often designed to remove phosphorus from wastewaters, it is evident from the literature that other pollutants can also be reduced significantly. Therefore, the objective of this research was a careful documentation of the relationships existing between the coagulation and flocculation parameters cited above and the degree of pollutant removal from domestic wastewaters. The pollutants selected for study were turbidity, suspended solids, total organic carbon, and total phosphorus.

CHAPTER II

THEORETICAL CONSIDERATIONS

Status of Chemical Clarification Design Procedures

Effective design of wastewater treatment systems requires knowledge of both the theoretical and practical principles involved. When given the problem to treat a municipal wastewater in a coagulation/sedimentation process, the engineer has many decisions to make. Among the variables which must be evaluated in light of the particular problem are:

- . the choice of coagulant
- . pH value during coagulation
- . duration of rapid mixing
- . intensity and duration of flocculation, and
- . optimum sedimentation time for floc removal

Many investigators have approached these considerations from a purely theoretical viewpoint or in laboratory studies using waters containing specially prepared suspensions. Among the major contributors are Dr. Thomas Camp (Camp, Dresser, and McKee, Boston, Mass.) on flocculation and sedimentation, and Dr. Werner Stumm (Harvard University, Cambridge, Mass.) on phosphorus aquo-chemistry and coagulation chemistry. While a comprehension of these underlying principles is essential to a complete understanding of the coagulation/ sedimentation process, the engineer also requires design oriented data which will allow proper selection of parameters for a particular wastewater treatment plant. Few investigators have presented data on coagulation processes which may be used directly by practicing engineers.

There are limited instances in the literature which show in any detail how selection of design parameters was accomplished. At the Lake Tahoe tertiary treatment plant (10)jar test data was used to determine the optimum lime dose for phosphorus removal and turbidity reduction. The pH which could be expected at that dose was also determined by the jar tests. Apparently no attempt was made to optimize removal efficiencies by varying the rapid mix conditions, flocculation speed or duration, or the sedimentation time.

In a similar case, design studies for an Environmental Protection Agency pilot plant to treat secondary effluent with lime at the Washington, D.C. Blue Plains plant (9) do not appear to have been guided by more than simple jar tests relating pollutant removal to lime dose. Design of a full scale lime addition to raw domestic wastewater treatment plant at Rochester, New York, was also based on limited jar test results (2).

The expense and time which would be required to conduct more extensive preliminary investigations prior to design of waste treatment facilities would be relatively small compared to the very large cost of the entire design/construction project. In addition, a better understanding of the principle variables should result in a superior design. Thus, the purpose of this research, in addition to investigating the relationships between coagulation conditions and pollutant removal, was to develop procedures and design guidance for the practicing engineer. It was hoped then that better designs can be produced either by using the data developed by this research, or by utilizing the laboratory techniques

proposed in the study.

Phosphorus Aquo-Chemistry

Domestic wastewaters normally contain about 6 to 10 mg/1 of phosphorus (as P). The largest single contributor is detergent phosphates which may account for from about fifty percent to as much as seventy percent of the total phosphorus. The remainder is phosphorus from human wastes and industrial processes.

Jenkins, et al. (24) has thoroughly reviewed the chemistry of phosphorus in water and the reactions of phosphorus species with metals such as those used as coagulants. In sewage and other natural waters phosphorus exists in the pentavalent state tetrahedrally coordinated with oxygen atoms or hydroxyl groups. Phosphates occur as orthophosphoric acid, as condensed phosphates in which two or more phosphorus atoms are joined by P-O-P bonds, or as organic phosphates in which P-O-C linkages are present. Each of these three forms may exist in solution or associated with particulate matter.

The anions of phosphoric acid and the most common condensed phosphates readily dissociate and behave as typical polyprotic acids. Based on a consideration of equilibrium constants and typical concentrations occuring in raw domestic wastewater, at pH 7.5 the predominant species are $H_2PC_4^-$, HPO_4^{2-} , $HP_3O_{10}^{4-}$, and $HP_2O_7^{3-}$. All these form dissolved ion pair complexes with metal ions. The concentration of dissolved phosphorus during precipitation will depend on chemical factors such as wastewater composition; the identity, stability, and growth kinetics of the precipitates; and on such physical parameters as temperature, flocculation rate and sedimentation efficiency. The chemical factors which affect phosphate coagulation with aluminum and calcium salts will be discussed in the next section. Flocculation and sedimentation will be discussed later in this chapter.

The salts of aluminum and calcium readily react with the phosphorus found in sewage. Aluminum salts are very easily hydrolyzed and their solutions show pH values similar to those of equimolar acetic acid solutions (28). The positive aluminum ion may be converted stepwise to the negative aluminate ion:

$$A1_{2}(SO_{4})_{3} \xrightarrow{2A1^{3+}} + 3SO_{4}^{2-}$$

$$A1^{3+} + H_{2}O \xrightarrow{A1OH^{2+}} A1OH^{2+} + H^{+}$$

$$A1OH^{2+} \xrightarrow{OH-in} A1(OH)_{4}^{-}$$

It has also been suggested that $Al_6(OH)_{15}^{3+}$ or $Al_8(OH)_{20}^{4+}$ is the most likely structure. In general, the chemistry of aluminum in water is not well understood, but it is known that the aluminum ion coordinates with water molecules and hydroxyl radicals and tends to form large polymeric molecules.

The solubility of phosphate in equilibrium with a solution containing excess A1(OH)₃ has been calculated from equilibrium data and is shown in Figure 1. This figure provides a good approximation of phosphate residuals because aluminum phosphate precipitation is thermodynamically and kinetically favored over aluminum hydroxide precipitation. Experimental



FIGURE 1--Equilibrium Solubility Diagrams for Aluminum and Calcium Phosphates (24).

results found by other researchers (24) and verified during this research show that the pH associated with the minimum residual phosphorus concentration is close to the thermodynamically predicted value of 6.0.

The interactions of condensed phosphates and aluminum have not been studied widely, but it is probable that adsorption as well as precipitation is an important removal mechanism in a mixture of orthoand condensed phosphates.

The presence of other common wastewater components has little direct effect on aluminum phosphate precipitation. Noting the strongly acidic effect on the aluminum ion in water, the buffering ability of bicarbonates will affect the final pH of the alum/wastewater mixture and thus affect the pH control system for the coagulation process.

The addition of hydrated, or slaked, lime $(Ca(OH)_2)$ to sewage serves both to raise the pH and to increase the calcium ion concentration. Thermodynamic calculations (24) show in Figure 1 that in the system $Ca^{2+} - PO_4^{3-} - CO_3^{2-} - H^+ - H_2O$ solubility decreases with increasing pH and that the precipitation of calcium carbonate competes with calcium phosphate (hydroxylapatite) precipitation between pH 9 and 10.5, but that hydroxylapatite precipitation by itself is responsible for the predicted low phosphate residuals between pH 7.5 and 8.5 and above 10.5.

While thermodynamic calculations of calcium phosphate and calcium carbonate precipitation from typical wastewater solution indicate that very low phosphorus residuals are possible ($\sim 0.05 \text{ mg/l}$ at pH 11.5), it is known that the precipitation of calcium phosphate is strongly influenced by both the kinetics of nucleation and crystal growth and by the chemical composition of the medium. Among the ions known to

influence the composition and solubility of precipitated calcium phosphate are H^+ , HCO_3^- , Mg^{2+} , and F^- . The net effect is to increase phosphate solubility at pH values below 9, but to decrease the solubility at higher pH values. At pH values above about 10.5 magnesium hydroxide is precipitated and the floc acts as an effective agent for increasing the settleability of suspended calcium phosphate particles. Alkalinity, and in general, the level of hardness, has a direct effect on coagulation/precipation chemistry since pH affects the chemistry of calcium carbonate precipitate, phosphorus precipitates, and magnesium hydroxide precipitate.

Wastewater Coagulation

The water and wastewater treatment process used to remove colloidal materials by addition of chemicals followed by a period of gentle mixing has been discussed in engineering literature using the terms "flocculation" and "coagulation". There is not at the present time complete agreement concerning the definitions of these terms. Following the terminology used by Weber (29), in this discussion coagulation will refer to the overall process of particle aggregation including both particle destabilization and particle transport. The term flocculation will refer to only the transport step.

Colloids may be considered to be that particulate matter which cannot be removed from suspension by gravitational settling within a practical period of time. Although most colloidal dispersions of concern in water and wastewater treatment are thermodynamically unstable, the rate of aggregation is slow and thus the coagulation process if used to increase the rate of aggregation.

When two similarly charged colloidal particles approach each other their diffuse layers begin to interact which always results in a repulsion force. In addition, all colloidal particles exert attractive forces for other particles. These forces are termed van der Waal's forces and can be pictured as the attraction which a positive nucleus has for electrons beyond its own radius. Their magnitude depends on the kinds of atoms in the colloid and the density of the particles. These forces decrease very rapidly as the distance separating the particles increases.

The net effect of charge and van der Wal's forces on colloid stability may be determined by summing the repulsive and attractive forces. This net interactive energy is shown in Figure 3 and may be considered as an activation energy which must be overcome for aggregation to occur. Its magnitude depends on the particle charge and on the ionic composition of the solution. At high ionic strength the energy barrier can be suppressed to such an extent that it disappears.

The particles in a colloidal dispersion are in constant motion and thus possess kinetic energy. The rate of coagulation is dependent on the magnitude of the energy barrier and the kinetic energy of the colloidal particles. Colloidal systems which have high activation energies and/or low kinetic energy will coagulate slowly compared to systems of low activation energy and/or high kinetic energy.

Colloid destabilization may be produced by four different mechanisms depending on the coagulant and the manner in which it is used.

Colloids owe their stability to charge and solvation effects of which charge effects are probably more important and at least are better understood. Stumm and Morgan (28) and Weber (29) have discussed the source of the surface charge and the conceptual model for colloid stability.

At pH values greater than about 3 the organic pollutants found in sewage possess a negative surface charge. This charge may be due to chemical reactions at the surface, lattice imperfections in the surface, or by ion adsorption. Because a colloidal dispersion does not have a net electrical charge, the primary charge on the particles must be counterbalanced in the aquous phase. As a result, an electrical double layer exists at every interface between a solid and water. This double layer consists of the charged particle and an equivalent excess of ions of opposite charge (counter-ions) which accumulate in the water near the surface of the particle. These counter-ions are attracted electrostatically to the region of the particle-water interface. The attraction results in a concentration gradient so that random thermal agitation can cause these ions to diffuse away form the particle surface and into the bulk solution where their concentration is lower. The result of these competing processes is a diffuse layer charge within which the concentration of counter-ions is greatest near the particle and decreases with increasing distance form the particle as shown in Figure 2.

Due to the presence of the primary charge an electrostatic potential exists between the surface of the particle and the bulk solution. The rate of decrease of this potential with increasing distance is affected by the number and type of ions in the bulk solution. At high ionic strength the potential decreases to zero in a short distance.



FIGURE 3--Schematic Illustration of Interaction Energy (29).

Double-layer compression. The only significant interactions are electrostatic in which ions of a similar charge to the primary colloid charge are repelled and counter-ions are attracted. The familiar Schulze-Hardy rule, which states that destabilization is brought about by ions of opposite charge and coagulation effectiveness increases markedly with charge, applies to this mode of coagulation. High ionic concentrations in the bulk liquid cause high counter-ions concentrations in the diffuse layer reducing its thickness. The activation energy barrier is reduced and may even disappear as shown in Figure 3. A mathematical treatment known as the VODL theory has been developed for this method of colloid destabilization. Weber (29) has pointed out that although this treatment describes simple electrostatic phenomena, systems of interest in water and wastewater treatment are not of this type since coagulants undergo many interactions in water solution and do not behave as simple ions. It is other destabilization mechanisms which are important in wastewater treatment.

Adsorption and charge neutralization. Coagulants of this type are typified by A1(III) and Fe(III) salts. As previously discussed, these metal ions in water do not exist as simple ions. When the solubility limit of the metal hydroxide is exceeded a series of hydrolytic reactions occur proceeding from simple complexes to the formation of a metal hydroxide precipitate. These hydroxo-metal complexes are readily adsorbed at interfaces. Conventional coagulation processes use quantities of A1(III) and Fe(III) which exceed the solubility of their metal hydroxides. It is presently thought that destabilization is brought about by metal polymers which are kinetic intermediates in the eventual

precipitation of a metal hydroxide precipitate.

In the pH range below the isoelectric point of the metal hydroxide positively charged polymers will prevail. Adsorption or these polymers can destabilize negatively charged colloids by charge neutralization. As may be expected from a consideration of the model presented, it is possible to overdose a colloidal suspension with metal ions causing restabilization with the colloids acquiring the opposite charge.

Aluminum salts can act as a coagulant in two ways. First, at low dosages destabilization occurs by adsorption. This method is characterized by long reaction times when colloid concentration is low. Thus, improvement in terms of coagulation time may be brought about by artificially introducing additional turbidity in the form of bentonitic clay or activated silica. Alternatively, higher Al(III) doses may be used as discussed below to cause entrapment in a "sweep floc" produced by the voluminous aluminum hydroxide precipitate. The required dose tends to decrease as the colloid concentration increases.

In considering the chemical aspects of colloid destabilization in sewage using Al(III) and Fe(III) salts, the principle factors are the coagulant dose and the pH. Since both act as fairly strong acids and the system is sensitive to pH level, pH control of the treatment process and the natural buffering capacity of the sewage are important design considerations. In sewage treatment an additional factor is that Al(III) will react first with the soluble phosphate, causing an "alum demand", and then act as a coagulant. As an example, the quantity of alum, $Al_2(SO_4)_3 \cdot 18H_2O$, required to precipitate five mg/l phosphorus would be 55 mg/l. Only after phosphorus precipitation occurs will colloid

destabilization take place.

Enmeshment in a precipitate. When high doses of alum, ferric chloride, or lime are added to colloidal suspensions the following reactions take place:

$$A1_2(SO_4)_3 \longrightarrow 2A1^{3+} + 3SO_4^{2-}$$

A1³⁺ + 30H[−] → A1(OH)₃♥

 \mathbf{or}

$$FeC1_3 \longrightarrow Fe^{3+} + 3C1^{-}$$

$$Fe^{3+}$$
 + $3OH^- \rightarrow Fe(OH)_3$

or

$$C_{a}(OH)_{2} \longrightarrow C_{a}^{2+} + 2OH^{-}$$
$$C_{a}^{2+} + CO^{2-} \longrightarrow C_{a}CO_{3}^{+}$$

Additionally, when magnesium is present and the pH is greater than about 10,

$$Mg^{2+} + 2OH \longrightarrow Mg(OH)_2$$

The solubility product constants for these reactions are (30):

$$\begin{array}{ccc} \frac{\text{Precipitate}}{\text{Al(OH)}_{3}} & \frac{\text{K}_{\text{sp}}}{3.7 \times 10^{-15}} \\ \text{Fe(OH)}_{3} & 1.1 \times 10^{-36} \\ \text{CaCO}_{3} & 8.7 \times 10^{-9} \\ \text{Mg(OH)}_{2} & 1.2 \times 10^{-11} \end{array}$$

In each case the solubility of the precipitate is very low so that under equilibrium conditions very little of the ionic species will be present. The precipitation of aluminum hydroxide is increased by the presence of sulfate ions when the pH of the solution is in the neutral or acid region.

Finally, because the colloidal particles serve as nuclei for precipitate formation, the rate of formation increases with increasing colloid concentration causing an inverse relationship between the optimum coagulant dose and the colloid concentration.

Adsorption and interparticle bridging. This category includes synthetic organic polymers which are described by the model developed by LaMer. That model states that the polymer molecule contains chemical groups which interact with sites on the surface of the colloidal particle. Some of the sites on the polymer molecule adsorb onto a colloidal particle surface with the remainder extending into the bulk solution. A second colloidal particle may attach to the extended polymer molecule forming a particle-polymer-particle bridge.

Treatment of wastewater with alum will result in destabilization of colloids by adsorption of aluminum species and by enmeshment in the aluminum hydroxide floc. Lime coagulation occurs through precipitation of calcium carbonate. If magnesium is present and the pH is sufficiently high, lime coagulation will be assisted by precipitation of magnesium hydroxide.

Wastewater Flocculation

The addition of metal salt coagulants to sewage will cause phosphorus to be precipitated. That precipitate forms a colloidal suspension

which may remain suspended, along with sewage colloids, if additional coagulant were not present to cause colloid destabilization. Destabilization will allow the colloids to agglomerate provided that interparticle contacts can be induced. One type of particle motion is naturally occurring Brownian motion (perikinetic flocculation). However, the energy available, and therefore the rate of interparticle contact, is small and so the rate of agglomeration is very slow. In practice, mechanical energy is added to the system to produce velocity gradients within the fluid which drive the particles together (orthokinetic flocculation).

The energy dissipated in a moving or stirred liquid is by shear within the liquid which results in the evolution of heat (31). The instantaneous shearing stress at a point is given by

$$\tau = \mu \, \frac{\mathrm{d}v}{\mathrm{d}s} \tag{1}$$

where $\frac{dv}{ds}$ is the absolute velocity gradient at the point and the constant μ is the absolute viscosity of the liquid. The root-mean-square velocity gradient is

$$G = \sqrt{\frac{W}{\mu}}$$
(2)

where W is the energy dissipated per unit volume and has been termed the dissipation function by Stokes. The value of w depends on the geometry of the rotors, stators (if any) and container, and on the speed of the rotors.

It has been shown by Camp and Stein (32) that the rate of particle agglomeration caused by motion of a fluid is directly proportional to the absolute velocity gradient. They also demonstrated that the absolute velocity gradient is equal to the square root of the ratio of the power loss by shear per unit volume of the fluid to the viscosity of the fluid. Although the velocity gradient at a point may vary considerably with time, under steady conditions of work input there is a mean velocity gradient that corresponds with the mean value of the rate of power dissipation throughout the tank and thus the mean rate of particle agglomeration. The following expression describes this relationship:

$$G = \left[\frac{P}{V\mu}\right]^{1/2}$$
(3)

Where G = root-mean-square velocity gradient

P = power input to the fluid

V = volume of the flocculator

 μ = absolute viscosity of the fluid

Camp (33) has noted that although the rate of floc formation is directly proportional to the velocity gradient, it does not follow that G may be increased to any level with resulting better pollutant removal. As the velocity gradient becomes greater the shearing forces increase and, since the larger the floc particle is the weaker it is, it will be more easily sheared apart. Thus, an equilibrium floc size exists within a system for each G value. To form small floc a large velocity gradient would be used and vice versa.

Following colloid destabilization, removal of wastewater particulates will involve flocculation and sedimentation. It is apparent that some
optimum value of G should exist which will produce the best result for a given suspension. At G values lower than optimum large rapidly settling agglomerates will be produced, but these low velocity gradients may not drive the particles together within a reasonable period of time. Also as the agglomerate grows it should remain suspended so that it can impact with other particles too small to settle out by themselves. Low G values may allow premature settling of floc. On the other hand, G values greater than the optimum will rapidly produce its equilibrium floc size, but the floc will be too small to rapidly settle out. The optimum design, then, will consider both the removal efficiency of the process and time required to accomplish the treatment. Common flocculation times are in the order of 5 to 15 minutes and sedimentation times 1 to 2 hours, so, for a given flow rate, factors which will minimize sedimentation tank size rather than flocculator size will have the major effect on the capital cost of a treatment plant.

In the study of flocculation it is important to be able to accurately determine the mixing intensity which is often expressed by the mean velocity gradient, G. In principle, it should be possible to determine G from tank dimensions, mixing paddle area, and paddle velocity. The power consumed during mixing would be expressed as the product of the drag force on the paddles multiplied by the paddle velocity, or

$$\mathbf{P} = \mathbf{F}_{\mathbf{D}} \mathbf{v} \tag{4}$$

where $F_D \approx$ paddle drag force v \approx paddle velocity

The drag force is

$$F_{D} = C_{D}A_{p} \frac{v^{2}}{2g}$$
(5)

where C_{D} = a drag coefficient

A = paddle area
 ρ = fluid density
 v = paddle velocity
 g = gravitational constant

Thus,

$$P = C_{D}A \rho \frac{v^{3}}{2g}$$
(6)

and, from Eq. (3)

$$G = \left[\frac{C_{D}^{A \rho v^{3}}}{2 \mu V g}\right]^{1/2}$$
(7)

The velocity, v, in this expression must be the actual paddle to water velocity rather than the absolute paddle velocity. Following an initial period of start-up the water will be moving in the same direction as the paddles, but at a somewhat lower velocity. Since it is not possible to directly observe the paddle-to-water velocity it is necessary to define a steady state proportionality constant, k

$$\mathbf{k} = \frac{\mathbf{v}}{\mathbf{a}} \tag{8}$$

where v = actual paddle to water velocity

a = observed paddle velocity

k = ratio of actual to observed velocities

and for a rotating shaft with paddle arms

and

$$a = r\omega \tag{9}$$

where r = length of paddle arm $\omega = \text{angular velocity of column shaft}$ $\omega = 2\pi s$ (10)

where s = rotational velocity of shaft in revolutions per second The result is an expression for the mean velocity gradient in terms of the observed shaft rotational velocity,

$$G = \left[\frac{4C_{D}^{A\rho k^{3} r^{3} \pi^{3}}}{\mu V g}\right]^{1/2} s^{3/2}$$
(11)

The principal difficulty in the application of Eq. (11) is in estimating a value for k. Although it has been assumed to be a constant, k will probably depend on factors such as paddle velocity and tank geometry, and an accurate estimate will be very difficult. Eq. (11) has value in establishing the form of the relationship between shaft rotational velocity and G, but is inadequate when G must be precisely determined.

An approach often adopted for determining G has been to indirectly measure the energy consumed during mixing by measuring the torque on the mixing shaft (31, 34). In this case Eq. (3) may be expressed as:

$$G = \left[\frac{T\omega}{\mu V}\right]^{1/2}$$
(12)

where T = net shaft torque after allowances for losses such as friction in bearings

Commercial torquemeters are available to make the necessary measurements.

Another approach which may be adopted is to measure the power consumed during mixing by measuring the amperage and voltage during operation of the mixing motor. This method has the advantages of simplicity and inexpensive equipment requirements. However, in addition to power expended during actual mixing, other losses in the motor, gear reducer, and shaft bearings will also be measured. If these losses are large compared to the mixing power consumption, it may be difficult to distinguish between the two, particularly at low mixing intensities.

CHAPTER III

JAR TEST EXPERIMENTS

Purpose

The overall purpose of this study was to investigate flocculation and clarification design parameters as applied to the chemically assisted primary sedimentation process. A major concern was an examination of the factors which control the removal of the algal nutrient phosphorus. From a consideration of effectiveness and economy, lime and alum are the most attractive coagulation chemicals in use today and were therefore selected for use in this study. Additionally, the colloid/coagulant interaction mechanisms of these two chemicals are different and represent two general classes of coagulants. The specific research goal during the jar test phase was to determine the effect of interactions between coagulant dose and pH during coagulation using a normal jar test procedure.

Experimental Methods and Materials

Design of coagulation systems requires evaluation of many process variables. Because of wide, complex variations in wastewater quality design of coagulation systems is usually accomplished through laboratory experiments which are then scaled up to plant size designs. The laboratory technique generally used is the jar test in which samples of the wastewater are batch treated to determine the optimum coagulant dose and pH. A major criticism of the jar test is that full-scale, flow-through systems are not adequately modelled by the small, batch jar test procedure. Because of the great difference in size the two are never geometrically similar so that the laboratory results may not be directly transferable to the field coagulation system.

The most common method for conducting jar test experiments has been to vary one parameter while holding the others constant. For example, first the pH may be varied at constant dose by addition of acid or base. The optimum pH will be that one giving the greatest removal of pollutants. With that optimum pH, the dose would then be varied to establish that optimum value. This approach assumes that each of the variables acts independently and that the researcher has adequate control of the experimental conditions so that changes in one variable will not inadvertently affect others. In many cases neither of these assumptions is valid. TeKippe and Ham (35) have found during coagulation of water with alum that the alum concentration and pH interact profoundly requiring both to be considered as independent variables. Also, because many coagulants behave as strong acids or bases and coagulation efficiency is often very sensitive to pH, it is very difficult to maintain sufficiently constant pH conditions while adding varying amounts of the coagulant.

An effective method of overcoming both of these problems is to present the data in two dimensional contour graphs as suggested by TeKippe and Ham (35) with the two independent variables as the axes and percent removal of the pollutant plotted on the graph. In this way when strong interactions exist between the variables this interaction can be shown by treating both variables as independent variables. In addition, exact pH control is not required since pH will be one of the independent variables. Examples of this procedure are presented later.

Prior to investigation of the coagulant dose/pH interaction by jar testing it was necessary to determine the conditions under which the jar tests would be conducted, i.e. intensity and duration of the rapid mix and slow mix steps and the duration of sedimentation. From a review of jar test procedures found in the literature and presented in Table 3, it was apparent that many combinations of these variables have been used. Based on these published values and preliminary tests, jar tests were conducted under the following conditions:

	Lime	Alum
Sample Size	l liter	l liter
Rapid Mix		
Intensity	100 rpm	100 rpm
Duration	2 min.	0.5 min.
Slow Mix		
Intensity	20 rpm	20 rpm
Duration	15 min.	15 min.
Sedimentation		
Duration	10 min.	10 min.

It may be noted that the only difference between lime and alum tests is the additional time required in the rapid mix step of lime tests. This is to allow the lime slurry time to dissolve. In contrast, alum solutions only need to be thoroughly mixed with the wastewater since alum is very soluble in water and can be added in concentrated solution form.

Sewage for both jar tests and the later column studies was obtained from the Amherst, Massachusetts, sewage treatment plant which serves

······································						·····	
			Rapid	Mix	Slov	w Mix	
Chemical	. Reference	Sample Size (liter)	Speed	Duration	Speed	Duration	Settling Duration
Lime	36	1.0	100 rpm	l min.	30 rpm	15 min.	30 min.
Alum	7	2.0	200 rpm	1.5 min.	20 rpm	12 min,	30 min.
Alum	37	0.8	228 rpm	l min.	19 rpm	15 min.	10 min.
Lime	10	0.5	100 rpm	0.5 min.	35 rpm	5 min.	60 min.
Al ³⁺ and F	e ³⁺ 38	0.5	90 rpm	2 min.	20 rpm	10 min. or more	20 min.
MgCO ₃	39	1.0	100 rpm	at least 2 min.	10 - 12 rpm	15 min.	20 min.
Fe ²⁺	40	1.5	90 rpm	2 min.	20 rpm	10 min.	2,5,15, 60, 120 min.
Lime	41	0,8	100 rpm	2 min.	30 rpm	20 min.	10 min.

÷ .

Table 3. Summary of Jar Test Procedures

.

۰.

the town of Amherst and the University of Massachusetts. Raw, degritted sewage was used in all studies. Early in the work sewage was transported in plastic carboys to the main Environmental Engineering laboratory. With the completion of pilot plant facilities adjacent to the Amherst treatment plant, sewage was then pumped directly from the primary clarifier center-well into the pilot plant building where jar tests and column studies were conducted.

Characteristics of Amherst sewage during these studies are shown in Table 4, together with typical sewage composition. Variability of the sewage from day to day was a factor which could not be controlled, so the results of each jar test or column test could not be compared precisely to other similar tests. In an effort to minimize this problem, comparisons were made on percent removal values rather than residual concentrations. In addition, since it was found that during periods of heavy rainfall, treatment plant flow rates increased significantly and the sewage at these times was weaker, no samples for jar tests or column experiments were obtained until flow conditions returned to those of normal dry weather flow.

Because the time required to analyze each of the samples for each of the test parameters would be a minimum of several days, a method was needed to preserve the samples. A review of the literature and laboratory tests showed that storage at 4°C was adequate. It was found that total phosphorus and total carbon values did not change appreciably, but that inorganic carbon and orthophosphate values increased by about 40 percent during the seven day test period. A slight decrease in TOC was observed since bacterial decomposition will continue even at this

	Amł	nerst Sewage	Typical Composition of Domestic Sewage (42)		
Parameter	Mean Value	Range of Values	Strong	Medium	Weak
Total Phosphorus, mg/l as P	5.5	1.7 to 8.0	20	10	6
Suspended Solids, mg/1	196	126 to 295	350	200	100
Turbidity, JTU	81	34 to 125.			
Total Organic Carbon, mg/l	148	85 to 275	300	200	100

· .

.

.

TABLE 4--Characteristics of Amherst Sewage

ω σ low temperature. Figure 4 shows the change in phosphorus and carbon during the test interval.

The parameters chosen to characterize the treatment process were total phosphorus, suspended solids, turbidity and total organic carbon (TOC). Total phosphorus was determined by the molybdenum blue colorimetric test developed by Jankovic, Mitchell and Buzzell (43). Ascorbic acid is the reducing agent used to produce the molybdenum blue complex. Because only orthophosphate will form the colored complex, total phosphorus was determined by first digesting the sample with potassium persulfate and sulfuric acid. The absorbance of the developed color was determined with a Bausch & Lomb Spectronic 20 spectrophotometer.

Suspended solids concentrations were determined using the membrane filtration technique described in Standard Methods (44). Turbidity was measured with a Hach Model 2100A turbidimiter.

Total organic carbon was determined using a Beckman Model 915 Total Organic Carbon Analyzer. Two determinations are made: total carbon (organic carbon plus carbonates) and inorganic carbon (carbonates). TOC is the difference between the two analyses performed on successive identical samples. Both analyses are based on conversion, in high temperature ovens, of sample carbon to carbon dioxide for measurement by a non-dispersive infrared analyzer.

Effects of pH and Alum Dose on Pollutant Removal

With the jar test procedures discussed above, alum (in the form of $Al_2(SO_4)_3$. $18H_2O$) was investigated to determine the effect of interactions



FIGURE 4--Effect of Sample Storage on Phosphorus and Carbon Determinations.

which occur between pH and dose. Alum was added to the jars of sewage as a concentrated solution. To obtain a number of different pH values for a given alum dose the pH was adjusted with solutions of sulfuric acid and sodium hydroxide added prior to the alum. Titration curves of alum/ sewage and acid (or base)/sewage were used to establish the amount of acid or base required to achieve the desired pH. Because pH is an independent variable when the results are plotted, exact control of pH was not necessary.

Following the settling portion of each jar test the pH was measured and a sample aliquot siphoned from just below the water surface of each jar. The result of the analyses for total phosphorus. suspended solids, turbidity, and total organic carbon is shown in Figures 5 through 8 in which the axes are alum dose and pH, and removal of each pollutant is present as the percent removal. The dashed line in each of these figures represents those jars in which no pH adjustment was made. Contour lines were then drawn connecting points of equal percent removal following the method suggested by TeKippe and Ham (35).

Several features of the plots are of interest. First, an area of optimum removal occurs at pH 5.9 and a dose of approximately 150 mg/l regardless of which parameter is used to evaluate performance. Second, the general appearance of the contour lines for total phosphorus, suspended solids, turbidity and TOC are very similar. In this regard, it may be noted that while TOC removal followed a somewhat different trend, the contour lines are still of the same general type. These similarities may be explained by further examining the meaning of each parameter selected for study. The removal of suspended solids



FIGURE 5--Percent Removal of Total Phosphorus Versus Alum Dose and pH. (Dashed Line Represents Samples Without pH Adjustment).



FIGURE 6--Percent Removal of Suspended Solids Versus Alum Dose and pH. (Dashed Line Represents Samples Without pH Adjustment).



FIGURE 7--Percent Removal of Turbidity Versus Alum Dose and pH. (Dashed Line Represents Samples Without pH Adjustment).



FIGURE 8--Percent Removal of Total Organic Carbon Versus Alum Dose and pH. (Dashed Line Represents Samples Without pH Adjustment).

(Figure 6) and turbidity (Figure 7) are closely related although the suspended solids measurement is predominantly large particles and turbidity is comprised of very small particles. Further, total phosphorus is a measure of three types of phosphorus compounds - soluble orthophosphate, polyphosphates, and organic phosphorus. The addition of coagulants precipitates the first two types as aluminum phosphate (29) which is then removed from suspension, along with the organic phosphorus, by the coagulant. Therefore, the total phosphorus removal plot (Figure 5) should, and does, look very similar to those for suspended solids and turbidity. Figure 8 showing removal of TOC appears to be slightly different because a significant portion of the TOC is in soluble form and not affected by the coagulation process. Thus, while the other parameters approach 100 percent removal, the TOC approaches some intermediate value reflecting the portion of the total which was in particulate rather than in a soluble form.

A feature of each of the plots is the occurrence of a "trough" of good removal values centered on pH 5.9 and beginning at alum doses of about 100 mg/1. The "trough" widens as the dose increases above 200 mg/1. It should be noted that relatively minor pH variations (greater than \pm 0.5 pH units) result in very large reduction in removal efficiency. This indicates that a process using alum as a coagulant would require careful pH control to operate properly. Although coagulation with iron compounds was not a part of this research, since the aqueous chemistry and mode of colloid destabilization are similar to alum, iron salts should also exhibit pH sensitivity when used as coagulants.

An interesting feature of the plots is an area of generally good contaminant removal extending from the "trough" of optimum removal toward lower alum doses and lower pH values. Thus at a pH of 4.5 to 5.0 moderate removal efficiency occurs at low doses of about 50 mg/l, but as the dose is increased at constant pH the removal efficiency decreases and then improves again as the dose is increased to greater than 150 mg/l. The most likely explanation for this behavior is that at low doses colloid destabilization occurs due to adsorption to produce charge neutralization. However, as the concentration of positively charged hydrolyzed aluminum increases, these charged species adsorb onto the negatively charged colloids to such an extent that charge reversal occurs resulting in a positively charged stable colloidal dispersion. This in turn causes an increase in suspended solids concentration together with a reduction in removal efficiency as compared to lower doses. As the dose is further increased, precipitation of aluminum hydroxide occurs and pollutant removal is accomplished by a precipitate enmeshment mechanism. This has often been termed "sweep floc".

A descriptive model has recently been proposed by Ferguson (45) to depict the alum coagulation process. The model consists of three cases and considers only the chemical reactions occurring between aluminum ions and orthophosphate ions.

In the first case the pH is near optimum and the aluminum/orthophosphate reaction occurs stoichiometrically. The optimum A1/P mole ratio is 1.4 to 1 and the reaction will be approximately 90 percent complete.

In the second case as more aluminum is added the precipitation reaction will become less efficient due to the solubility of Al/P mole ratio exceeds the range of 1.4 to 1.6 then the phosphorus residual is controlled by the solubility of aluminum phosphate, $A/P0_4$. At Al/P ratios greater than 1.6 the phosphorus residual is controlled by the combined solubility of aluminum phosphate and aluminum hydroxide.

The third case considers that at any pH value the limit on phosphorus removal is due to the solubility of aluminum phosphate and aluminum hydroxide. This minimum phosphorus concentration is in the order of 10^{-6} mole per liter.

The application of this model to the data developed in this research is somewhat lin ited since Ferguson's model considers only reactions between aluminum and the orthophosphate ion rather than reactions of other phosphorus species such as the condensed phosphates and particulate phosphorus species present in domestic sewage. A second limitation is that many other ions occur in sewages and will affect the predicted solubility relationships. Thirdly, the model considers only the insolublization of orthophosphate and not the entire removal process including separation of the precipitate from the water phase by flocculation. In order for comparisons to be made between this model and coagulation of sewage it would be necessary to determine the relative amounts of orthophosphate and other phosphorus species. For the data gathered in this research, if it can be assumed that one-half of the total phosphorus concentration is in the form of orthophosphate, then the Al/P ratio is approximate 4.5 to 1 for

optimum phosphorus removal. This very high ratio compared to that predicted by the model is due to the additional requirement of aluminum ions to destabilize both the colloids already present in the sewage and those formed by the precipitation of $A/P0_{4}$.

Based on this alum jar test work the following conclusions were made:

For Amherst sewage the optimum alum dose is about
 150 mg/l and the optimum pH is 5.9.

2. The coagulation mechanism for Amherst sewage may be either adsorption and charge neutralization, or precipitate enmeshment depending on the dose and pH. For dose and pH conditions close to those found to be optimum, the removal mechanism is precipitate enmeshment.

3. When using alum as a coagulant, careful pH control is required to limit the range to about 0.5 pH units either side of pH 5.9.

Effects of pH and Lime Dose on Pollutant Removal A similar jar test program was conducted using lime (CaO) as the coagulant. These results are shown as Figures 9 through 12, again depicting the removal of total phosphorus, suspended solids, turbidity, and TOC. The behavior of lime as a coagulant is quite different from that of alum. Lime acts as an enmeshment precipitate throughout the entire region studied (29). Removal efficiency continuously increases as both lime dose and pH increase with no optimum conditions observed. It should be noted that high doses of lime or high pH alone will not result in effective treatment; this



FIGURE 9--Percent Removal of Total Phosphorus Versus Lime Dose and pH. (Dashed Line Represents Samples Without pH Adjustment).



FIGURE 10--Percent Removal of Suspended Solids Versus Lime Dose and pH. (Dashed Line Represents Samples Without pH Adjustment).



FIGURE 11--Percent Removal of Turbidity Versus Lime Dose and pH. (Dashed Line Represents Samples Without pH Adjustment).



FIGURE 12-Percent Removal of Total Organic Carbon Versus Lime Dose and pH. (Dashed Line Represents Sample Without pH Adjustment).

only occurs when both high dose (greater than 300 mg/l as CaO) and high pH (greater than 11) occur together. Both conditions are needed because the precipitating species, predominantly calcium carbonate, decreases in solubility as the pH increases. The addition of lime provides both the necessary calcium ions and the high pH simultaneously since, when it is hydrated, lime forms $Ca(OH)_2$ which is a strong base. Carbonate ions are present due to the natural alkalinity of the wastewater. Additionally, at pH values greater than 10, $Mg(OH)_2$ is precipitated and adds to the settleability of the floc.

A summary to serve as a comparison between alum and lime jar results is presented in Table 5. These data were obtained from Figures 5 through 8 for alum treatment and from Figures 9 through 12 for lime treatment. The procedure was, first, to note the percent removal values on Figures 5 through 8 corresponding to an alum dose of 175 mg/l at pH 5.9, and on Figures 9 through 12 the values corresponding to a lime dose of 400 mg/l at pH 12.0. Then, secondly, the residual concentrations associated with the percent removal values were obtained by refering to the original raw data of the jar tests. Although it may seem from this limited data that perhaps lime treatment is to be preferred, the differences observed are due more to variations in characteristics of the raw sewage than to differences in the treatments. It is not possible from this data to conclude that either lime or alum treatment would result in a more efficient process than the other. Additionally, a review of the literature previously shown in Tables 1 and 2 has indicated that, at optimum dose and pH

TABLE 5--Summary of Jar Test Results

	Alt	um*	Lime ^{**}		
	% Removal	Residual Concentration	<u>% Removal</u>	Residual Concentration	
Suspended Solids	93	10 mg/1	84	28 mg/l	
Turbidity	86	8.5 JTU	88	7.7 J'TU	
Total Organic Carbon	64	40 mg/l	77	20 mg/l	
Total Phosphorus	83	1.0 mg/1	95	0.3 mg/l	

* Dose 175 mg/l (as (Al₂(SO₄)₃·18 H₂O); pH 5.9
** Dose 400 mg/l (as CaO); pH 12.0

conditions, the effectiveness of the two treatments is very similar.

Several additional aspects of lime treatment of raw sewage were investigated. It has been reported in the Environmental Protection Agency Process Design Manual for Phosphorus Removal (46) that it is possible to obtain good removal efficiency at relatively low lime doses and low pH values. At Richmond Hill, Ontario, the use of 175 mg/l lime resulted in a pH of 9.3, and removal of 78 percent of the BOD and 83 percent of the total phosphorus. Also, Tofflemire and Hetling (21) were able to achieve removal of 76 percent of the COD and 91 percent of the suspended solids at a pH of 10.8. However, jar testing with Amherst sewage showed considerably lower removals occur at a similar dose (see Figures 10 and 12). It is apparent from the data that the Richmond Hill sewage contained somewhat more alkalinity than Amherst sewage (75 to 150 mg/l as CaCO₃) which may account for some of the difference. The mixed domestic and industrial waste used by Tofflemire and Hetling had an alkalinity of 150 mg/l.

In recent studies reported by Ketchum and Weber (41) it was shown that chemical coagulation of low alkalinity waters with lime could be improved by the addition of activated silica. However, the upper limit of alkalinity where activated silica addition allowed a reduction in the required lime dose was only about 50 mg/l. It is unlikely that municipal wastewaters would contain such a low alkalinity. Thus, the use of activated silica in conjunction with lime for treatment of sewage appears unlikely.

As an aid to lime coagulation Wuhrmann (23) reported the use of small concentrations of ferric iron. Settleability of hydroxylapatite and calcium carbonate flocs were shown to be greatly improved by this technique. In an effort to improve turbidity removal, particularly at lower lime doses, jar tests were performed using varying lime doses and varying ferric iron doses. The results are tabulated in Table 6. It is apparent from this data that the coagulation of Amherst sewage with lime is not aided by the addition of small doses of ferric iron and that higher ferric iron doses may actually increase residual turbidity values.

In another attempt to in prove lime coagulation, both the Lake Tahoe tertiary treatment plant (10) and the Blue Plains advanced waste treatment plant (9) recycled settled lime sludge. This, in addition to improving the removal efficiencies, also reduced carbonate scaling problems. At Lake Tahoe approximately 20 mg/l settled lime sludge was added to the flocculation basin to increase phosphorus removal. At Blue Plains the benefit of sludge recycle was a decrease in scale buildup on piping following the clarifier.

As a part of this study-jar tests were run to determine the effect of recycling lime sludge on turbidity and phosphorus removal. These results are presented in Table 7. At low flocculation duration (less than 10 minutes) large doses of recycled sludge resulted in increases in settled turbidity and phosphorus. When the flocculation time was greater than 10 minutes recycling solids seemed to have no effect even at a recycle rate of 250 mg/l. In no case could it be concluded

Lime Dose mg/l	Measured pH	Fe ³⁺ Dose mg/1	• Turbidity JTU
0	-	0	71
50	. 9.9	0	65
100	10.55	0	65
150	11.2	0	59
200	11.45	0	28
250	İ1.65	0	17
300	11.65	0	17
$2 mg/1 Fe^{3+}$	Added 2 Minutes Afte	r Lime Addition	
0	-	2	120
50	10.35	2	120
100	11.1	2	120
150	11.3	2	120
200	11.65	2	54
250	11.9	2	29
300	11.95	2	27
Varying Fe ³	⁺ Dose Added 2 Minute	es After Lime Dose	
0	-	0	92
300	11.95	0	28
300	11.95	1	28
300	11.9	3	31
300	11.85	6 5	37
300	11.85	10	30
300	11.75	20	37

-

TABLE 6--Jar Test Results Using Line and Ferric Iron

Sludge Added			Flocculation Time (min.)		
ml	mg / 1	5	10	20	30
0	0	8.6*	5.2	3.8	3.7
1	13	8.5	5.0	3.5	3.3
5	63	8.9	4.6	4.0	3.8
20	250	13	4.5	3.7	3.2

TABLE 7--Effect of Adding Settled Sludge to Lime Jar Tests

Residual Turbidity

Residual Phosphorus

Sludge Added			Flocculation Time (min.)			
ml	<u>mg / l</u>	5	<u>10</u>	20	<u>30</u>	
0	0	0.70**	0.54	0.36	0.28	
1	13	0.56	0.45	0.31	0.29	
5	63	0.70	0.42	0.36	0.33	
20	250	0.92	0.47	0.40	0.38	

* **Residual Turbidity in JTU Residual Total Phosphorus in mg/l as P

Jar Test Conditions

Rapid Mix 2 minutes at 100 rpm Slow Mix 25 rpm for varying time Settling 10 minutes Lime Dose 400 mg/l at pH 12.25 Return sludge was obtained by treating raw sewage with 400 mg/1 lime. The return sludge Total Suspended Solids was 12,600 mg/l.

that the addition of sludge to the flocculation zone had a beneficial effect.

Based on the lime jar test work the following conclusions were made:

1. In contrast to alum coagulation, rather than observing an optimum condition of dose and pH, removal efficiency with lime increases continuously as the dose and pH are increased.

2. When treating Amherst sewage lime and alum were found to produce comparable results.

3. Low pH lime coagulation was not successful in treating Amherst sewage due to the low alkalinity present.

4. The use of ferric iron did not improve removal efficiency.

5. Recycling of lime sludge was found to not be effective in producing an effluent having lower phosphorus or turbidity.

CHAPTER IV

COLUMN EXPERIMENTS

Purpose

Jar testing, as discussed in the previous chapter, established the optimum dose and pH for removal of pollutants from sewage using alum and lime as coagulants. In the second phase of study design criteria for the flocculation-clarification process were obtained using a batch column equipped with mixing paddles. The purpose of these studies was to relate mixing speed during flocculation to pollutant removal efficiency following sedimentation.

Experimental Equipment

Flocculation-sedimentation studies were conducted in a batch column one foot in diameter and eight feet in height as shown in Figure 13. This equipment consisted of a cast acrylic (Plexiglas) tank fitted with sample points along one side. The tank was constructed in three sections for ease of fabrication and later handling, and was supported by a wooded frame which was secured to the wall of the pilot plant building. A mixer shaft of 3/4-inch aluminum rod extended along the axis of the tank and was prevented from horizontal movement by a socket hole in the tank bottom slightly larger than the shaft diameter. Aluminum mixing blades consisting of strips of aluminum sheet were attached to the shaft parallel to the tank axis by horizontal aluminum rods. The weight of the shaft and mixing blades was supported by a silicon rectifier (SCR) controlled 1750 rpm DC motor with a 10/1 worm



FIGURE 13--Flocculation/Sedimentation Column,

gear reducer. With the rheostat control device, rotational velocity could be maintained at any value between 0 and 175 rpm.

When the tank was initially used it was found that little effective mixing was accomplished due to rotation of the entire fluid mass. The remedy chosen was to install baffles inside the tank to increase eddy currents. These baffles consisted of four one-inch strips of aluminum sheet extending the entire height of the column and held in place by circular rings of aluminum sheet at the top and bottom of the column.

One purpose of column testing was to relate the mixing intensity during flocculation, as measured by the mean velocity gradient, G, to the efficiency of the flocculation-sedimentation process. To do this it was necessary to measure the mean velocity gradient in the tank. The means chosen was to measure the electrical input to the DC motor armature which in turn was a measure of the power being consumed to turn the mixing paddle. In addition to the power used to mix the tank contents, power was also consumed in the gear reducer and in the shaft socket at the bottom of the tank.

Power consumption was measured by an ammeter and voltmeter attached across the input to the motor armature. Motor speed was measured by a generator tachometer supplied by the motor manufacturer. At low paddle speeds the shaft rotational velocity was determined visually.

The expression relating shaft rotational velocity to the mean velocity gradient, G, has been previously developed as Eq. (11).

$$G = \left[\frac{4C_{D}A_{\rho k}^{3}r_{\pi}^{3}}{\mu Vg}\right]^{1/2} S^{3/2}$$

If G, as determined from electrical power measurement, is plotted versus shaft rotational velocity on log-log paper the result should be a straight line with a slope of 1.5.

For the system used in the column studies the measurement of power consumption included that actually consumed in mixing the fluid and other losses in the gear reducer and the socket at the bottom of the shaft. To separate the mixing power from the losses, power consumption readings were made with the column empty and with it filled with tap water. These two sets of values were subtracted to determine the useful power. These values were then plotted on log-log paper as shown in Figure 14. The result is the expected straight line but with a slope of 1.67. Although the slope is not in exact agreement with the theoretical value of 1.5, it does indicate that the methods employed were correct.

In spite of the demonstrated correct approach to relating G to shaft rpm, the results were not completely satisfactory because G values below about 60 sec⁻¹ could not be determined by this technique. The major factor preventing the measurement of G of less than 60 sec^{-1} is that gear power consumption was a large portion of total power consumption, particularly at low rpm, and thus the

ύ 1


FIGURE 14--Column Flocculation Calibration Curve Relating Mixing Intensity to RPM.

substraction of column full and column empty power usage resulted in the subtraction of two large, nearly equal values. At low rpm it was not possible to differentiate between the two power values. Although extrapolation could extend the relationship to lower rpm values, that procedure would lead to questionable G values.

Values of G commonly used in water treatment plants have been summarized by Camp (33) as in the range of 29 to 74 sec⁻¹ with the median of the 20 values he presents being 39 sec⁻¹. Similar data presented by Walker (47) indicates for eight water treatment plants a maximum of a 145 sec⁻¹, and a minimum of 33 sec⁻¹. Thus, G values of interest in wastewater treatment plants will be in the range of 20 to 150 sec⁻¹ and the inability to accurately measure G values below 60 sec⁻¹ with the experimental equipment was an unfortunate shortcoming of this method of mean velocity gradient measurement.

In addition to the column in which flocculation and sedimentation occurred, other portions the apparatus included a rapid mix tank, a pump to transfer the sewage/coagulant mixture from the rapid mix tank to the column, and an electrical control panel. The arrangement of the equipment is shown in Figure 15.



ł

Column Test Procedure

Prior to column testing, jar tests had been performed to determine the optimum coagulant dose and pH for both alum and lime. In the case of alum, that optimum was found to be a dose of 175 mg/1 (as $Al_2(SO_4)_3$. 18 H₂O) at a pH of 5.9. In contrast, lime does not exhibit an optimum dose and pH. Greater doses produce higher pH values and better removal efficiency. Further, lime doses for the column tests were selected to be 300 mg/1 and 400 mg/1, values which are typical of doses applied in the treatment of sewage.

Column tests were run as a batch system. Sewage was pumped from the centerwell of the Amherst sewage treatment plant primary clarifier to the adjacent University of Massachusetts pilot plant facility. For each run the coagulant and G value were selected prior to the run. Coagulant was added to the raw, degritted sewage in the rapid mix tank and mixed with a one-sixth horsepower mixer for one minute in the case of alum and two minutes with lime. Following the rapid mix period the mixture was pumped into the flocculation/sedimentation tank, flocculated at the known G value for 10 minutes, and allowed to settle. Based on preliminary column testing the sedimentation step was terminated after visual observations indicated that sedimentation was essentially complete. During jar testing work the sedimentation time was taken to be 10 minutes. In column studies 45 minutes was selected initially, but when it became

apparent from analysis of the data that a longer settling time would yield data which could be more easily evaluated, the sedimentation time was increased to one hour. During the sedimentation period samples were withdrawn from the column at various depths and at time intervals, and measured in terms of the same four pollutional parameters that were studied during the jar test phase, total phosphorus, suspended solids, turbidity, and TOC. To illustrate the procedure used in data analysis, a sample set of data obtained in one experiment is presented in Table 8.

The percent removal values were then plotted against their respective depths and times as shown in Figure 16 for the suspended solids data of Table 8. Smooth curves may then be drawn through points of equal percent removal. Design curves were then developed in a manner similar to that described by Camp (48) for discrete settling and discussed by Eckenfelder and O'Connor (49) for flocculant settling.

The percent removal by sedimentation of a particulate pollutant at a given time is equal to the sum of a) the particles which have settled to the tank bottom, in the given time, plus b) a portion of each other slower settling particle group equal to the ratio the actual particle settling velocity divided by the theoretical settling velocity of a particle which will just settle out in the given time. In practice, the calculation is most easily performed by substituting the particle settling depth rather than velocity assuming that all particles started at the surface. In equation form this would be:

% Removal =
$$P_1 + P_2 \frac{D_2}{D_T} + P_3 \frac{D_3}{D_T} + \dots + P_N \frac{D_N}{D_T}$$

TABLE 8--Settling Analysis of Coagulated Raw Sewage

Test Conditions:

Lime Dose 400 mg/l pH 11.85 Rapid Mix Time 2 minutes Flocculation Time 10 minutes Flocculator Speed 5 RPM (G~5 sec⁻¹)

Time	Depth from Top	Sus _j So	oended lids	Tur	bidity	тс	DC	Tota	al P
(min.)	(ft.)	Conc.	% Rem.	Conc.	% Rem.	Conc.	% Rem.	Conc.	% Rem.
Initial		244	-	79	-	105	÷-	3.8	-
0	1	266	- 9	66	16	97	8		-
0	3	248	-2	66	16	93	11	-	- 1
0	5	280	-15	76	4	113	-8	-	-
0	7	280	- 15	76	4	93	11	<u></u>	-
15	1	111	55	18	77	66	37	0.35	91
15	3	134	45	23	71	67	36	0.48	88
15	5	133	45	26	67	68	35	0.87	77
15	7	156	36	34	57	73	30	0.64	83
30	1	46	81	12	85	62	41	0.28	93
30	3	42	83	12	85	б 1	42	0.18	95
30	5	60	75	13	84	55	48	0.37	90
30	7	65	73	19	76	63	40	0.38	90
45	1	29	88	12	85	62	41	0.13	97
45	3	39	84	14	85	60	43	0.30	92
45	5	39	84	12	85	60	43	0.10	97
-15	7	35	86	15	81	57	46	0.23	9-1
00	1	16	93	11	86	60	43	0.25	93
60	3	31	87	11	86	61	42	0.19	95
60	5	23	91	11	86	60	43	0.10	97
60	7	33	86	12	85	60	43	0.10	97



FIGURE 16--Percent Removal of Suspended Solids Versus Column Depth and Sedimentation Time for Example Data.

where % Removal = Total percent removal in the given
tank in the given time

$$P_1, P_2, \dots, P_N = Particle \text{ groups}$$

 $D_1, D_2, \dots, D_N = Depths to which particle groups P_1,$
 P_2, \dots, P_N have settled assuming the
particles started at the surface
 $D_T = Total depth of tank$

An example of this calculation is shown in Table 9 for a 21 minute sedimentation time with the data in Figure 16. By selecting a time where the settling curve crossed the time axis the calculations are made somewhat easier. Similar calculations were performed at the other times where a percentage removal line crossed the time axis at the eight foot depth. Those results are shown in Table 10. Also shown in Table 10 is the corresponding sedimentation tank overflow rate which is calculated as follows:

OR, in
$$\frac{\text{gal/day}}{\text{ft}^2}$$
 = (settling velocity, in $\frac{\text{ft}}{\text{hr}}$) (7.48 $\frac{\text{gal}}{\text{ft}^3}$) (24 $\frac{\text{hr}}{\text{day}}$)

The data of Table 10 was then plotted as a curve relating percent removal to overflow rate at the given G value as shown in Figure 17.

The purpose of constructing these curves was to determine whether the removal of pollutants in a coagulation/sedimentation system is affected by the intensity of flocculation, G, within the range of values normally encountered in coagulation systems. It was postulated that an optimum G value might be found. That is, a G values less than optimum

Time	% S.S. Range	Depth Settled (ft.)	Depth Ratio	% S.S. Removed
21 min.	0-40	8	1.0	40.0
	40-50	6.3	0.79	7.9
	50-60	3.6	0.45	4.5
	60-70	2.3	0.29	2.9
	70-80	1.4	0.18	1.8
	80-90	0.6	0.08	0.8
				57.9

TABLE 9--Percent Removal of Suspended Solids at Varying Time

TABLE 10--Settling Time vs. Percent Removal and Overflow Rate

Time	Percent Removal	Settling Velocity	Overflow Rate
21 min.	57.9	22.9 ft/hr	[*] 4111 gpdsf
30	74.2	16.0	2872
35	81.5	13.7	2459
37	83.7	13.0	2334
41	85.6	11.7	2100
62	90.0	7.7	1382

* $(22.9 \frac{\text{ft}}{\text{hr}}) (7.48 \frac{\text{gal}}{\text{ft}^3}) (24 \frac{\text{hr}}{\text{day}}) = 4111 \text{ gal.} /\text{day/ft}^2$



FIGURE 17--Overflow Rate Versus Percent Removal of Suspended Solids for Example Data.

the precipitate particles would not obtain sufficient kinetic energy to be driven together, and at excessively high G values the shearing forces would break down the floc into particles too small to readily settle out.

Column Test Results

The column test phase of this study was designed to determine if the percent removal of the pollutional parameters is significantly affected by the flocculation G value used. The range of G values employed was $5 \text{ to } 40 \text{ sec}^{-1}$. Although a calibration curve was prepared (Figure 14) there are uncertainties about low G values resulting from the inability to accurately measure power consumption at low mixing intensities. Thus, the results are reported here in terms of mixing shaft rpm rather than G values. The approximate G values for the shaft rpm are:

<u>RPM</u>	<u>G, sec</u> 1
5	5
10	15
15	30
20	60
25	80
30	100
40	170

The percent removal of each pollutant parameter as a function of overflow rate for each rpm value investigated is presented in Figures 18 through 21 representing results obtained when alum was used as the coagulant, whereas Figures 22 through 29 were derived from column



FIGURE 18--Percent Removal of Total Phosphorus Versus Overflow Rate for Alum Dose of 175 mg/l at pH 5.9.



FIGURE 19--Percent Removal of Suspended Solids Versus Overflow Rate for Alum Dose of 175 mg/l at pH 5.9.



FIGURE 20--Percent Removal of Turbidity Versus Overflow Rate for Alum Dose of 175 mg/l at pH 5.9.

-

.



FIGURE 21--Percent Removal of Total Organic Carbon Versus Overflow Rate for Alum Dose of 175 mg/l at pH 5.9.



FIGURE 22-Percent Removal of Total Phosphorus Versus Overflow Rate for Lime Dose of 300 mg/l.



FIGURE 23--Percent Removal of Total Phosphorus Versus Overflow Rate for Lime Dose for 400 mg/l.



FIGURE 24--Percent Removal of Suspended Solids Versus Overflow Rate for Lime Dose of 300 mg/l.



FIGURE 25--Percent Removal of Suspended Solids Versus Overflow Rate for Lime Dose of 400 mg/l.



FIGURE 26--Percent Removal of Turbidity Versus Overflow Rate for Lime Dose of 300 mg/1.



FIGURE 27--Percent Removal of Turbidity Versus Overflow Rate for Lime Dose of 400 mg/l.



FIGURE 28--Percent Removal of Total Organic Carbon Versus Overflow Rate for Lime Dose of 400 mg/l.





tests using lime. In examining each figure, the rpm value producing the highest percent removal of the specified parameter at a given overflow rate is the optimum rpm value. If turbidity and total phosphorus removal are examined for alum dosing experiments (using in each case a dose of 175 mg/l at a pH of 5.9) there appears to be a tendency toward slightly better performance at low flocculation speeds (5 rpm or $G \sim 5 \text{ sec}^{-1}$). However, the removal of suspended solids and TOC do not confirm this relationship. Thus, it is not possible to definitely conclude that low mixing intensities produce better results on the basis of all four parameters observed. Better results at lower mixing speeds may be due to slight real differences or may be due to some unmeasured variable which is characteristic of the sewage. In either case it is clear that when alum is used as a coagulant to treat raw sewage, mixing intensity is a relatively unimportant design parameter. Indeed, jar testing illustrated the very significant effect of coagulant dose and pH and these would probably far outweight mixing intensity in importance for an actual design application.

Similar data analysis of experiments in which lime was used as the coagulant at dosages of 300 mg/l and 400 mg/l again did not show that a particular mixing intensity produced the best results for all parameters. In the cases of Figures 24, 26, 28 and 29 the graph of the 30 rpm values produced better results. However, if that were the optimum value it should follow that values near 30 rpm should also yield good results and that mixing intensities either much greater or much less than 30 rpm should yield the poorest results. Unfortunately, no such trend exists, as illustrated by examination of the turbidity removal

shown in Figures 26 and 27. Thus, it was concluded that lime treatment of raw sewage, as well as alum treatment, is relatively insensitive to mixing intensity for the test conditions used.

One possible explanation for the insensitivity of pollutant removal to mixing intensity may be that the flocculation time of 10 minutes was sufficiently long that flocculation was successfully completed in all cases regardless of how low the value of G was during each experiment. Further studies varying the duration of flocculation, particularly at low duration, say one or two minutes, would indicate whether this explanation is in fact the case. If it could be shown that even 10 minutes flocculation is sufficient to bring about efficient flocculation over a wide range of G values, then further consideration of G as a principle design variable could be eliminated. Even in a large scale treatment process the expense would be relatively small for a flocculation tank with only a 10 minute detention period, or perhaps even less if studies could show that, say five minutes is sufficient.

A second consideration is that the flocculation mixing intensity must be sufficient to prevent deposition of solids in the mixing zone. From the column settling data including that shown in Table 8 it was apparent that this lower limit on mixing intensity when using alum is about 15 rpm (G ~ 30 sec⁻¹) and when using lime about 20 rpm (G ~ 50 sec⁻¹). Although mixing intensity did not appear to be a critical design factor, several other significant process design features are evident from examination of Figures 18 through 29. Differences in clarification behavior between alum and lime treatment of raw sewage can be readily seen. The dependence of percent removal of a pollutant on overflow rate is shown by the slope of the line for the given flocculation conditions. That is, a steeper slope implies that removal efficiency is more sensitive to overflow rate. Comparison of the graphs obtained in the alum and lime experiments illustrate that alum coagulation produces a suspension that settles less readily than that of lime coagulation. Thus, in an alum coagulation process there exists a greater possibility for upset due to hydraulic variations or convection currents. Design of alum coagulation processes should therefore be more conservative than those for lime coagulation.

A summary of column test results is presented in Table 11. For this comparison overflow rates yielding approximately the same percent removal for alum and the two lime doses were selected: 1750 gpdsf for alum treatment and 3000 gpdsf for lime treatment. The percent removals of the pollutant parameters at these overflow rates are also comparable to published percent removal values as seen by comparing Table 11 with Tables 1 and 2. Residual pollutant values were obtained, as in the preparation of Table 5,

	$\frac{\text{Alum}^{*}}{\text{OR} = 1750 \text{ gpdsf}}$		Lime (300 mg/l as CaO)** OR = 3000 gpdsf		$\frac{\text{Lime (400 mg/l as CaO)}^{***}}{\text{OR} = 3000 \text{ gpdsf}}$	
	% Removal	Residual Concentration	% Removal	Residual Concentration	% Removal	Residual Concentration
Suspended Solids	75	65 mg/l	73	65 mg/1	72	70 mg/1
Turbidity	88	13 JTU	75	20 JTU	82	14 JTU
Total Organic Carbon	47	75 mg/l	40	65 mg/l	43	65 mg/l
Total Phosphorus	85	1.0 mg/1	89	0.25 mg/l	89	0.4 mg/l

TABLE 11--Summary of Column Test Results

*Dose 175 mg/l (as Al₂(SO₄)₃·18 H₂O); pH 5.9 **Lime Treatment pH approximately 11.8 ***Lime Treatment pH approximately 12.0

by referring to the original raw data in this case obtained during column testing.

When comparing the data in Table 11 to similar data for jar testing (Table 5) it is apparent that jar testing produced better results, particularly in terms of suspended solids and turbidity removal. During jar testing with either alum or lime residual suspended solids concentrations in the range of 10 to 30 mg/l were easily achieved. Turbidity residuals less than 10 JTU were often observed. In contrast, during column testing residual values were about twice those obtained during jar testing.

Because a floc particle was considered to be removed when it had settled to the bottom of the jar (5-inches) or below the lowest port of the column (7-feet), some of the difference may be attributed to different settling distances. But, more importantly, the settling conditions within the jar and column were seen to be different. During jar testing very little turbulence was observed more than a few minutes after flocculation was completed and the floc rapidly settled out. In the column, on the other hand, considerable turbulence was observed resulting from temperature induced density currents and also due to displacement of water by settling solids. These conditions also occur in the jar tests, but the differences in scale made the effects considerably more pronounced in the column. Consequently, it should be expected that column testing would produce higher pollutant residual concentrations

than jar tests due to these scale factors. Continuous flow clarifiers, in addition to problems of internal currents of the type discussed above, also suffer from hydraulic short circuiting thereby further reducing removal efficiency.

The overflow rates chosen for the above comparisons were 1750 gpdsf for alum and 3000 gpdsf for lime. By comparing the removals at these overflow rates in Table 11 with the published values from pilot and field scale operations (Tables 1 and 2), it is seen that the removal efficiencies are comparable, but the overflow rates found in this study are considerably higher. Eckenfelder has recommended that when designing continuous clarifiers the overflow rates found in batch studies be reduced by a factor of 1.25 to 1.75. If the larger of these factors is applied to the overflow rate values found in this study then the values resulting closely approximate overflow rates being used today.

The column testing shows that the design of alum coagulation processes should be more conservative than lime processes both because lower overflow rates are needed and because hydraulic variations are more likely to upset alum processes. Although the data is limited, it appears from Table 2 that these differences are not generally appreciated. That is, from Table 2 it can be seen that clarifier overflow rates for lime and alum processes have been very similar. Therefore, it should be concluded that in the design of flocculation-sedimentation processes to treat domestic sewage more emphasis should be placed on proper selection of overflow rates and less consideration on mixing intensity provided a minimum flocculator mixing intensity is furnished to prevent deposition of solids.

Characterization of Lime and Alum Sludges

One of the major expenses at any sewage treatment plant is disposal of the sludge produced. Since chemical coagulation of raw sewage is relatively new, little data exists concerning the quantity or characteristics of the sludge. Therefore, as the column studies were being conducted the quantity of sludge produced was noted. This data is presented in Table 12 and Figure 30. The quantity of sludge when using alum is seen to rise sharply from about 2% to 6% by volume as the mixing speed is increased. Lime sludge volume seems also to exhibit a slight rise in volume as the mixing speed increased. Both lime sludges averaged 1.8 percent by volume, or about 40 percent of the average alum sludge volume. A comparison of initial suspended solids concentration with sludge volume indicates that sludge volume is independent of the initial suspended solids concentration within the range of the values encountered.

One of the most important considerations in sludge disposal is volume reduction, usually accomplished by gravity thickening and then removing unbound water by vacuum filtration, centrifugation, or sand bed drying. A procedure commonly used to characterize sludges for these applications is the specific resistance and coefficient of compressibility test (⁵⁰, ⁵¹). Measurements of specific resistance and coefficient of compressibility for sludges obtained from the settling column are presented in Table 13. Two lime doses, 300 mg/l and 400 mg/l, were used and one alum dose of 175 mg/l at pH 5.9. The values found for the specific resistance of the two lime sludges were very similar. Those of the alum sludge were approximately three times as great. This means that, other factors being equal, it would take three times as long to dry

TABLE 12--Sludge Volume in Column Tests

·

		*
Lime	Column	Test

	Sludge Depth	Sludge Volume	Initial Suspended Solids
300 mg/1			
5 RPM	3.1 cm.	1.3%	246 mg/1
10 RPM	3.1	1.3	
15 RPM	5.6	2.3	202
20 RPM	4.0	1.7	
30 RPM	4.6	2.0	199
400 mg/1			
5 RPM	2.5	1	244
10 RPM	3.4	1.4	
15 RPM	5.6	2.3	228
20 RPM	4.3	1.8	
30 RPM	5.0	2.1	185
40 RPM	5.0	2.1	
	Alum C	olumn Test ^{**}	
5 RPM	5.0	2,1	194
15 RPM	10.0	4.2	263
25 RPM	12.1	5.1	295
40 RPM	14.3	6.0	261

*60 Minutes Settling

.

^{***}45 Minutes Settling; 175 mg/l at pH 5.9



FIGURE 30--Column Mixing Speed Versus Sludge Volume.

Specific Resistance (sec ² /m)							
Sludge	$\Delta P = \frac{12.6 \text{ cmHg}}{12}$	$\Delta P =$ 25.4 cmHg	$\Delta P = 41.6 \text{ cmHg}$	Coefficient of Compressibility			
Lime, 300 mg/1	2.52×10^9	5.08 x 10 ⁹	7.47 x 10^9	0.909			
Lime, 400 mg/l	2.72×10^9	4.77×10^9	7.50×10^9	0.858			
Alum, 175 mg/1 pH 5.9	7.96 x 10 ⁹	13.83 x 10 ⁹	20.15 \times 10 ⁹	0.778			

TABLE 13--Sludge Dewatering Characteristics

•

..- ---

.

- -- --

the alum sludge on the sand beds and, since the theoretical relationships are different with mechanical dewatering devices, 1.73 times as long when using a vacuum filter or centrifuge. The specific resistance and coefficient of compressibility values compared well with published values for similar types of sludges (50, 51).

CHAPTER V

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Summary

The treatment of domestic wastewater with chemical processes, rather than biological, is becoming increasingly popular as the effectiveness, ease of control, and relative economy of these processes is established. One of the most promising processes is chemically assisted primary treatment using inorganic coagulants such as alum or lime to remove the algal nutrient phosphorus as well as to increase removal of suspended solids and oxygen demanding materials. Optimum design and operation of these facilities requires proper selection of several design parameters, namely choice of coagulant, dose, pH, flocculation intensity and duration, and sedimentation time. The current literature does not indicate either the best values for these parameters or a rational methodology for determining them.

During this investigation the coagulation process for treatment of raw domestic sewage was studied using jar tests and a column flocculation-sedimentation apparatus. In the first phase a jar test procedure was established to determine the effect on the removal of pollutants of interactions between coagulant dose and pH during coagulation. The pollutants studied were total phosphorus, suspended solids, turbidity, and total organic carbon. Numerous jar tests conducted under varying dose and pH conditions were plotted to show the optimum values for both alum and lime. It was found that for the wastewater studied alum coagulation exhibits optimum removal at a dose of about 175 mg/l and a pH of 5.9. Small variations in pH either above or below the optimum were found to have a large effect on pollutant removal. Lime coagulation did not have an optimum value in that pollutant removal increased continuously as the dose and pH increased. Other process variables such as coagulation at low lime dose, use of ferric iron as a coagulant aid, and sludge recycling were also studied.

The second phase of the research was an investigation of the effect of flocculation mixing intensity and sedimentation time on pollutant removal using the best pH and dose conditions found in the first phase. An apparatus was designed and fabricated in which flocculation could be conducted using a known, measured mixing intensity and then settled in the same column. Alum and lime were used to investigate the combined effect of varying flocculation and sedimentation. The intensity of flocculation was found to be a relatively unimportant design parameter when compared to overflow rate, dose, and pH for both chemicals provided that enough energy was applied to prevent floc particle settling during the flocculation period. Alum was shown to produce a lighter, slower settling floc than lime which would require that alum coagulated water overflow rates be lower to produce a comparable result. Alum floc will also be more susceptible to process upsets due to hydraulic variations.

The sludges produced by column testing were characterized in terms of the volume of sludge produced and its dewatering characteristics. Alum sludge was found to be more voluminous than lime sludge and was more difficult to dewater.
Conclusions

Methodology for the design of wastewater coagulation processes is not well developed and consists of simple jar testing to determine the optimum dose and pH. No consideration has been given to determining by laboratory tests the best values of flocculation intensity and sedimentation time.

An improved jar test procedure following that of TeKippe and Ham can more effectively determine the proper coagulant, dose, and pH for each particular wastewater. It was found that alum coagulation exhibits a narrow zone of optimum pollutant removal, whereas in lime coagulation processes efficiency increases continuously as pH and dose increase. Alum coagulation will require careful pH control to prevent variations due to changes in wastewater flow and characteristics.

Coagulation in a low lime process, use of ferric iron as a coagulant aid for lime processes, and recycling of lime sludge were all found to be unsuccessful in treating the low alkalinity Amherst sewage.

Flocculation mixing intensity was found to be less important than overflow rate in column studies. Other very important process variables were coagulant dose and pH. Mixing intensity levels need only be maintained sufficiently high to prevent deposition of floc.

Lime floc are more dense than those of alum and thus allow higher clarifier overflow rates and are less affected by hydraulic fluctuations. Current clarifier design procedures apparently do not appreciate these differences.

98

Alum floc volume was greater than that of lime under similar conditions and was found to increase with increasing mixing speed while lime floc did not. Alum floc is also more difficult to dewater.

Recommendations

Recommendations for future studies and design of wastewater treatment coagulation facilities can be made from this investigation. <u>Future studies</u>. Future studies should extent these investigations to wastewaters of higher alkalinity. Many important differences will probably be noticed including lower pH for a given lime dose which, together with more bicarbonates present, should produce a higher quality effluent. Higher alkalinity may also allow the use of the low lime process and encourage the use of ferric iron as a coagulant aid. On the other hand, the difficulties encountered in this research may not all be due to low alkalinity and may be caused, at least in part, by other factors which should be identified.

If further column studies are undertaken to further define the effect of mixing intensity on pollutant removal, a torque meter should be used between the gear reducer and the water level. This method of power measurement, although more expensive, would be considerably more accurate, particularly at low mixing intensity.

Continuous flow studies should be conducted to verify the conclusions of this research on waters of varying composition and to determine scale-up factors for the design of flocculators and clarifiers. One interesting possibility would be to run parallel processes using lime in one and alum in the other to evaluate process control for each. During

99

these experiments the effect of varying the duration of flocculation should be investigated since it may be possible to show that, given even a relatively short time, the effect of varying G values will not affect pollutant removal.

The methodology and results of this study should be applied to the coagulations of other colloidal suspensions such as those encountered in the treatment of drinking water.

Design recommendations. Jar tests should always be conducted using the method discussed by TeKippe and Ham and used in this research. Although additional jars must be used and additional analyses run, a great amount of additional information can be derived and the results have more validity.

When sewage treatment plants are to be designed which use a coagulation process, both jar tests and column tests should be conducted to evaluate the critical parameters. The additional time and expense will result in a superior design and will be minor compared to the cost of the plant itself.

If alum is used for coagulation of sewage, an effective pH control system should be used since alum coagulation is very sensitive to pH variations.

Assuming that effectiveness and cost are equal, lime coagulation would be the better choice than alum because of easier process control, higher clarifier overflow rates, fewer clarifier upsets due to a more dense floc, and a lesser sludge volume which can be more easily dewatered.

VITA

Stuart P. Bowen was born December 31, 1942 in Southbridge, Massachusetts. He attended Mary E. Wells High School in Southbridge. In 1964 he received a Bachelor of Science Degree in Civil Engineering from Worcester Polytechnic Institute in Worcester, Massachusetts. Following graduation he worked for Metcalf and Eddy, and for Whitman and Howard in the years 1964 to 1967. In 1967 he completed a Master of Science in Sanitary Engineering from Northeastern University, Boston, Massachusetts, on the cooperative education program.

From 1967 to 1969 he worked as an environmental engineer for Monsanto Company in Texas City, Texas.

In 1969 he entered the Environmental Engineering Program in the Civil Engineering Department at the University of Massachusetts for the Degree of Doctor of Philosophy.

Beginning in August 1973 he became associated with JBF Scientific Corporation, Burlington, Massachusetts.

He is a member of Sigma Xi, The American Society of Civil Engineers, the Water Pollution Control Federation, and the American Water Works Association.

Alum Dose mg/l	Measured pH	Turbidity JTU	Suspended Solids mg/l	Total Organic Carbon mg/1	Total Phosphorus mg/l
0	3,55	60	68	85	
0	5.2	49	61	84	6.6
0	6.0	46	70	78	5.5
0	6.5	45	69	74	6.5
0	6,95	45	82	71	6.5
50	4.35	50	57	76	5.1
50	5,25	22	38	59	3.5
50	5,85	51	89	75	6.6
50	6.3	51	89	72	5.4
50	6.7	51	89	76	5,4
75	4.8	30	30	60	3.8
75	5.65	15	16	53	1.6
75	6.1	39	63	67	4.3
100	4.8	35	35	51	3.9
100	5.65	8.2	18	52	1.6
100	6.0	19	27	47	2.9
100	6.3	50	71	67	4.6
100	7.05	55	83	73	6.0
125	5.55	17	15	43	2.1
125	5.9	7.1	5	42	1.4
125	6.25	14	17	45	2.0

TABLE A-1--Jar Test Results with Aluminum Sulfate $[A1_2(SO_4)_3 \cdot 18 H_2O]$ as Coagulant

--- --

Alum Dose mg/l	Measured . pH	Turbidity JTU	Suspended Solids mg/l	Total Organic Carbon mg/l	Total Phosphorus mg/l
150	5.0	49	72	56	4.5
150	5.0	11	14	40	0.9
150	6.0	11	12	43	0.75
150	6.3	21	22	45	1.6
150	6.6	-42	75	53	4.4
175	5.9	8.3	9	41	1.1
175	6.1	16 ·	20	41	1.8
175	6.4	20	36	46	2.3
200	5.2	31	47	47	2.6
200	5.75	9.7	12	37	1.1
200	6.65	27	40	49	2.3
200	8.35	28	55	51	
250	5.05	19	26	38	1.4
250	5.75	4.4	12	35	0.8
250	6.45	15	28	42	1.3
Raw Sewage		58	135	115	6.4

TABLE A-1--Jar Test Results with Aluminum Sulfate $[Al_2(SO_4)_3 \cdot 18 H_2O]$ as Coagulant (Continued)

-

- --

Lime Dose mg/l	Measured pH	Turbidity JTU	Suspended Solids mg/1	Total Organic Carbon mg/l	Total Phosphorus mg/l
0	7.3	44	106	61	5.8
0	7.45	39	86	47	4.2
0	8.86	39	120	52	5.0
0	9.95	42	89	62	4.6
0	12.5	25	95	48	4.6
100	6,75	55	90	44	5.0
100	8.5	45	108	51	1.4
100	9.7	30	79	40	2.4
100	10.4	45	89	49	3.5
100	10.75	51	94	59	2.1
100	11.7	5 Ì	103	54	4.2
100	12.45	33	96	40	3.4
200	6.2	60	91	55	2.9
200	9.4	33	57 ⁻	35	1.2
200	10.8	23	61	30	0.9
200	11.75	25	74	41	1.0
200	12.0	21	62	35 .	1.1
200	12.3	19	56	29	1.0
300	6.75	51	55	47	4.4
300	9.4	24	71	29	0.4
300	10.95	13	40	24	0.6
300	11.6	26	51	27	0.4

TABLE A-2--Jar Test Results with Lime (CaO) as Coagulant.

Lime Dose mg/l	Measured pH	Turbidity JTU	Suspended Solids mg/l	Total Organic Carbon mg/l	Total Phosphorus mg/l
300	12.1	7.9	28	31	0.6
300	12.4	12	34	25	0.7
400	7.15	41	57	38	4.0
400	9.4	20	38	25	0.5
400	10.0	14	42	23	0.7
400	11.3	7.7	17	19	0.4
400	11.8	7.7	28	20	0.1
400	12.15	6.4	23	28	0.4
500	7.6	22	39	20	2.5
500	9.7	12	33	24	0.4
500	11.0	12	41	21	0.2
500	11.65	12	26	21	0.2
500	11.95	6.2	21	16	0.3
500	12,35	4.0	24	29	0.3
Raw Sewage	7.2	62	175	87	5.8

TABLE A-2-- Jar Test Results with Lime (CaO) as Coagulant. (Continued)

Time min.	Sample Depth feet	Turbidity JTU	Suspended Solids mg/l	Total Organic Carbon mg/l	Total Phosphorus mg/l
Initial	Value	85	194	100	5.1
5	1	47	241	129	5.4
5	3	91	233	85	6.3
5	5	75	147	84	3.8
5	7	78	156	102	5.0
10	. 1	76	195	117 .	5.6
10	3	65	146	85	4.1
10	5	65	156	98	3,1
10	7	73	143	82	3.3
20	1.	40	90	66	1.7
20	3	47	89	73	2.1
20	5	64	134	93	3.7
20	7	6 9	114	81	3.2
30	1	17	26	55	0.5
30	3	22	49	. 65	0.8
30	5	32	71	56	1.7
30	7	66	127 .	78	3.8
45	1	· 11	20	49	0.4
45	3	12	46	60	0.2
45	5	14	21	48	0.2
45	7	22	61	63	1.3

TABLE A-3--Column Test Using Alum: Dose 175 mg/1, pH 5.9, Mixing Speed 5 RPM

•

106

- -

- - - -

• • • • • • • • • •

•

Time min.	Sample Depth feet	Turbidity JTU	Suspended Solids mg/l	Total Organic Carbon mg/l	Total Phosphorus mg/l
Initial	Value	105	262	134	7.2
5	1	110	2 82	115	7.5
5	3	96	230	123	6.6
5	5	105	252	142	6.7
5	7	110	286	157	8.0
10	1	82	168	97	5.7
10	3	83	151	63	6.1
10	5	105	185	93	4.8
10	7	110	256	114	4.1
20	1	45	99	67	2.4
20	3	6 2 [·]	131	88	3.9
20	5	72	152	87	4.4
20	7	98 [°]	228	129	6.1
30	1	29	34	66	1.0
30	3	34	27	65	1.1
30	5	70	125	90	4.0
30	7	88	185	108	5.7
45	1	12	8	62	0.8
45	3	18	14	56	0.3
45	5	27	35	69	0.7
45	7	60	98	86	3.1

.

TABLE A-4--Column Test Using Alum: Dose 175 mg/l, pH 5.9, Mixing Speed 15 RPM.

1

Time min.	Sample Depth feet	Turbidity	Suspended Solids mg/l	Total Organic Carbon mg/l	Total Phosphorus mg/l
Initial	Value	108	276	142	6.7
5	1	105	244	132	6.2
5	3	105	262	135	7.2
5	5	110	304	153	6.8
5	7	110	294	148	6.4
10	1	85	190	124	5.4
10	3	86	194	123	5.7
10	5	105	266	149	8.0
10	7	110	291	134	7.3
20	1	49	76	80	2.9
20	3	66	156	:00	3.7
20	5	88	186	134	6.7
20	7	105	281	146	3.2
30	1	25	50	7 6	1.5
30	3	42	91	98	2.2
30	5	64	151	107	3.0
30	7	105	276	136	8.2
45	1	12	11	57	0.6
45	3	21	59	65	1.4
45	5	23	12	68	1.3
45	7	57	70	95	4.4

TABLE A-5--Column Test Using Alum: Dose 175 mg/l, pH 5.9, Mixing Speed 25 RPM.

- -- •

•

٠

. .

- --

Time min.	Sample Depth feet	Turbidity JTU	Suspended Solids mg/l	Total Organic Carbon mg/l	Total Phosphorus mg/l
Initial	Value	110	245	140	8.3
5	1	110	224	133	8.7
5	3	110	237	138	7.5
5	5	110	273	140	8.6
5	7	110	245	148	8.3
10	1	· 96	195	117	7.0
10	3	105	234	126	7.5
10	5	110	277	140	8.5
10	7	110	248	158	8.7
20	1	57	108	98	3.0
20	3	95	208	111	7.8
20	5	110	267	135	8.8
20	7	110	236	148	8.8
30	1	30	42	68 .	0.8
30	3	46	39	66	1.9
30	5	100	244	132	2.6
30	7	110	230	141	8.9
45	1	15	13	60	0.9
45	3	29	16	62	1.9
45	5	34	36	67	0.4
45	7	105	227	116	7.3

TABLE A-6Column	Test Using Alum:	Dose 175	mg/1, pH 5.9,
	Mixing Speed 40	RPM.	

,

· -

- -

. -

,

Time min.	Sample Depth feet	Turbidity JTU	Suspended Solids mg/1	Total Organic Carbon mg/l	Total Pho sphorus mg/l
		76	257	117	2.0
Initial	Values	75	234	105	1.6
		77	247	113	2.1
0	1	61	253	93	
0	3	71	272	88	
0	5	82	311	102	
0	7	80	323	104	-
15	1	25	106	71	0,32
15	3	29	120	67	0.27
15	5	34	152	6 9	0,29
15	7	45	176	76	0.61
30	1	17	42	59	0.10
30	3	17	55	6 0 ΄	0.10
30	5	20	68	63	0.13
30	7	23	48	60	0.10
45	1 .	15	52	59	0.18
45	3	15	55	57	0.29
45	5	17	42	58	0.11
45	7	18	60	58	0.20
60	1	15	50	59	0.17
60	3	16	56	56	0.13
60	5	16		61	0.19
60	7	17	51	58	0.14

TABLE A-7--Column Test Using Lime: Dos 300 mg/l; pH 11.8; Mixing Speed 5 RPM

.

.

~

· ..

-

•-

Time min.	Sample Depth feet	Turbidity JTU	Suspended Solids mg/l	Total Organic Carbon mg/1	Total Phosphorus mg/l
	· ·	75	185	96	4.1
Initial	Values	77	213	83	3.6
		75	209	92	3.4
0	1 .	87	266	101	
0	,3	88	269	. 96	• - -
0	5	88	278	120	
0	7	91	317	122	
15	1	31	107	67	0.56
15	3	35	111	68	0.55
15	5	42	148	76	0,65
15	7	52	168	86	1.03
30	ì	21	59	59	0.30
30	3	22	66	61	0.43
30	5	27	84	64	0.38
30	7	30.	95	62	0.38
45	1	20	18	59	0.28
45	3	20	18	61	0.23
45	5	21	35	58	0.20
45	7	22	41	58	0.35
60	1	19	20	58	0.30
60	3	19	23	56	0.30
60	5	21	34	59	0.25
60	7	20	34	56	0.30

TABLE A-8Column	Test Using Lime	: Dose 300 mg/l;	pH 11.95;
	Mixing Speed 15	RPM.	

.

.

Time min.	Sample Depth feet	Turbidity JTU	Suspended Solids mg/l	Tctal Organic Carbon mg/l	Total Phosphorus mg/l
<u></u>		83	198	132	2.4
Initial	Values	80	194	143	1.1
		81	206	151	2.6
0	1	102	377	140	
0	3	105	391	159	
0	5	101	396	155	
0	7	102	383	145	· `
15	1	38	107	72	0.36
15	3	40	138	80	0.56
15	5	48	144	82	0.88
15	7	88	277	113	2.43
30	1	12	24	58	0.13
30	3	16	24	59	0.22
30	5	17	30	61	0.12
30	7	20	37	61	0.17
45	1	8.8	8	55	0.09
45	3	10.0	14	55	0.04
45	5	11	15	59	0.11
45	7	12	28	58	0.04
60	1	8.3	5	54	0.06
60	3	9.0	9	54	0.04
60	5	9.4	10	54	0.06
60	7	9.5	14	57	0.15

TABLE A-9--Column Test Using Lime: Dose 300 mg/l; pH 11.9; Mixing Speed 30 RPM.

Time	Sample Depth	Mixing Speed			
min.	feet	10 RPM	20 RPM	40 RPM	
		77	75	88	
Initial Values		75	75	85	
		76	78	88	
0	1	102	106	110	
0	3	101	105	114	
0	5	110	110	113	
0	7	112	111	114	
15	1	32	37	62	
15	3	34	40	57	
15	5	43	48	97	
15	7	52	100	111	
30	1	14	14	22	
30	3	17	17	24	
30	5	18	16	31	
30	7	21	22	29	
45	1	12	9.1	. 12	
45	3	· 12	11	15	
45	5	13	12	15	
45	7	14	12	14	
60	1	12	8.5	8.9	
60	3	12	8.5	9.1	
60	5	12	8.5	9.1	
60	7	12	9.0	9.6	

· .

TABLE A-10--Column Test Using Lime: Dose 300 mg/l; pH 11.65-11.9 Turbidity Values.

___ ·

,

Time min.	Sample Depth feet	Turbidity JTU	Suspended Solids mg/l	Total Organic Carbon mg/l	Total Phosphorus mg/l
		80	227	92	4.9
Initial	Values	77	264	118	2.6
		81	240	105	4.0
0	1	66	266	97	
0	3	66	248	93	
0	5	76	280	113	
0	7	76	280	93	
15	1	18	111	66	0.35
15	3	23	134	67	0.48
15	5	2 6	133	ó8	0.87
15	7	34	156	73	0.64
30	1	12	46	62	0.28
30	3	12	42	61	0.18
30	5	13	60	55	0.37
30	7	19	65	63	0.38
45	1	12	29	62	0.13
45	3	12	39	60	0.30
45	5	12	39	60	0.1
45	7	15	35	57	0.23
60	1	11	16	60	0.25
60	3	11	31	61	0.19
60	5	11	23	60	0.1
60	7	12	33	60	0.1

TABLE A-11--Column Test Using Lime: Dose 400 mg/l; pH 11.85; Mixing Speed 5 RPM

-

- -

•

-- -

- - --

Time min.	Sample Depth feet	Turbidity JTU	Suspended Solids mg/l	Total Organic Carbon mg/l	Total Phosphorus mg/l
		75	237	106	3.7
Initial	Values	73	205	125	3.3
		71	243	111	2.4
0	1	82	321	128	
0	3	82	333	122	
0	5	85	351	125	
0	7	84	386	131	
15	1	24	109	73	0.15
15	3	25	126	84	0.6
15	5	31	106	86	1.3
15	7	72	284	105	1.4
30	1	8.4	60	65	0.18
30	3	9.1	61	65	0.23
30	5	11	63	62	0.18
30	7	16	85	67	0.23
45	1	6.5	39	61	0.18
45	3	7.0	46	61	0.20
45	5	7.9	54	61	0.18
45	7	11	61	62	0.25
60	1	6.1	53	60	0.18
60	3	6.5	41	62	0.20
60	5	6.6	42	60	0.20
60	7	7.3	35	61	0.35

TABLE A-12--Column Test Using Lime: Dose 400 mg/l; pH 11.85; Mixing Speed 15 RPM.

··· ___ ---

-

Time min.	Sample Depth feet	Turbidity JTU	Suspended Solids mg/l	Total Organic Carbon mg/l	Total Phosphorus mg/l
		67	188	115	1.2
Initial	Values	65	180	102	2.5
		68	186	107	1.4
0	1	87	301	119	 ,
0	3.	88	317	110	
0	5	87	326	119	
0	7	87	342	113	
15	1	27	87	6ž	0.46
15	3	30	102	65	0.47
15	5	38	154	69	1.1
15	7	72 ·	259	95	1.4
30	1	7.8	51	54	0.06
30	3	11	57	56	0.05
30	5	14	64	55	0.12
30	7	16	66	56	0.10
45	1	7.0	47	54	0.08
45	3	6.0	32	53	0.02
45	5	7.2	44	52	0.04
45	7	9.8	55	55	0.08
60	1	5.1	21	55	0.03
60	3	. 5.9	8	55	0.03
60	5	6.0	. 30	54	0.02
60	7	6.9	40	52	0.02

TABLE A-13--Column Test Using Lime: Dose 400 mg/l; pH 12.1; Mixing Speed 30 RPM

.

· · · - - - - --

- -

~

•

• •

Time	Sample Depth	Mixing Speed			
min.	feet	10 RPM	20 RPM	40 RPM	
		62	71	87	
Initial Values		63	76	88	
		65	72	87	
0	1	72	. 98	104	
0	3	77	99	106	
0	. 5	87	99	104	
0	7	90	105	104	
15	1	17	31	49	
15	3	28	38	55	
15	5	28	39	60	
15	7	39	63	100	
30	1	5.9	7.6	12	
30	3	7.3	9,3	16	
30	5	8.4	9.9	17	
30	7	8.9	14	22	
45	1	5,2	6.1	7.7	
45	3	5.4	6.5	7.5	
45	5	5.4	6.8	8.6	
45	7	6.2	7.1	8.5	
60	1	3.7	5.6	7.0	
60	3	3.9	5.7	7.1	
60	5	4.0	5.9	6.8	
60	7	3.9	5.9	7.3	

TABLE A-14--Column Test Using Lime: Dose 40 mg/l; pH 11.8-12.0; Turbidity Values

_ ___

. -

1

--

- - - -

BIBLIOGRAPHY

- Tossey, D., et al., "Tertiary Treatment by Flocculation and Filtration." Jour. San. Eng. Div., Proc. Amer. Soc. Civil Engr., 96, SA1, 75 (1970).
- Weller, L. W., and Wahbeh, V.N., "Design of Wastewater Treatment Plant Additions at Rochester, N.Y." presented at 45th Annual Conf. of Water Poll. Control Fed., Atlanta, Ga. (1972).
- 3. Sawyer, C.N., "Biological Engineering in Sewage Treatment." Sew. Work's Jour., 16, 925 (1944).
- Rudolfs, W., "Phosphates in Sewage and Sludge Treatment, II. Effect on Coagulation, Clarification, and Sludge Volume." <u>Sew.</u> Works Jour., 19, 178 (1947).
- 5. Owen, R., "Removal of Phosphorus from Sewage Plant Effluent with Lime." Sew. and Ind. Wastes, 25, 548 (1953).
- 6. Lea, W.L., et al., "Removal of Phosphates from Treated Sewage." Sew. and Ind. Wastes, 26, 261 (1954).
- 7. Malhotra, S.K., et al., "Nutrient Removal from Secondary Effluent by Alum Flocculation and Lime Precipitation." Int. Jour. of Air and Water Poll., 8, 487 (1964).
- 8. <u>Cleaning Our Environment The Chemical Basis for Action</u>, American Chemical Society, Washington, D.C. (1969).
- 9. O'Farrell, T.P., et al., "Advanced Waste Treatment of Washington, D.C." U.S. Dept. of the Interior, Federal Water Pollution Control Administration, Advanced Wastewater Treatment Research Laboratory (1969).
- South Tahoe Public Utility District, "Advanced Wastewater Treatment as Practical at South Tahoe." Environmental Protection Agency Project No. 17010 ELQ, Washington, D.C. (1971).
- 11. Graeser, H.J., and Haney, P.D., "Dallas Builds Center to Study Wastewater Reclamation." Water & Wastes Eng., 5, 34 (1968).
- 12. "Summary Report-Advanced Waste Treatment, July 1964 July 1967." Federal Water Pollution Control Administration Report No. WP-20-AWTR-19 (1968).

- - -- ----

- Buzzell, J.C., and Sawyer, C.N., "Removal of Algal Nutrients from Raw Wastewater with Lime." Jour. Water Poll. Control Fed., 39, R16 (1967).
- Albertson, O.E., and Sherwood, R.J., "Phosphate Extraction Process." Jour. Water Poll. Control Fed., 41, 1467 (1969).
- Schmid, L.A., and McKinney, R.E., "Optimization of Phosphorus Removal with Lime Treatment." Univ. of Kansas Publ., Bull. of Engr. and Arch. No. 58, 49 (1968).
- 16. Spohr, G., and Talts, A., "Phosphate Removal by pH Controlled Lime Dosages." Public Works, 63 (1970).
- Weber, W.J., Jr., et al., "Physicochemical Treatment of Wastewater." Jour. Water Poll. Control Fed., 42, 83 (1970).
- Nesbitt, J.B., "Phosphorus Removal The State of the Art." Jour. Water Poll. Control Fed., 41, 701 (1969).
- Eliassen, R., and Tchobanoglous, G., "Chemical Processing of Wastewater for Nutrient Removal." Jour. Water Poll. Control Fed., 40, R171. (1968).
- 20. van Vuuren, L.R.J., et al., "Advanced Purification of Sewage Works Effluent Using a Combined System of Lime Softening and Flotation." Water Research, Pergamon Press, 463 (1967).
- Tofflemire, T.J., and Hetling, L.J., "Treatment of a Combined Wastewater by the Low-Lime Process." Jour. Water Poll. Control Fed., 45, 210 (1973).
- 22. Shindala, A., and Stewart, J.W., "Chemical Coagulation of Effluents from Municipal Waste Stabilization Ponds." <u>Water and</u> Sew. Works, 118, 100 (1971).
- 23. Wuhrmann, K., "Objectives, Technology, and Results of Nitrogen and Phosphorus Removal Processes." In <u>Advances in Water Quality</u> <u>Improvement</u>, E.F. Gloyna and W.W. Eckenfelder [Ed.], <u>University of Texas Press</u>, Austin, Texas (1968).
- Jenkins, D., et al., "Chemical Processes for Phosphate Removal." Water Res., 5, 369 (1971).
- Mulbarger, M.C., et al., "Lime Clarification, Recovery, Reuse, and Sludge Dewatering Characteristics." Jour. Water Poll. Control Fed., 41, 2070 (1969).

- Roberts, J. M., and Roddy, C.P., "Recovery and Reuse of Alum Sludge at Tampa." Jour. Amer. Water Works Assoc., 52, 857 (1960).
- 27. Albrecht, A. E., "Disposal of Alum Sludges." Jour. Amer. Water Works Assoc., 64, 46 (1972).
- 28. Stumm, W., and Morgan, J. J., "Chemical Aspects of Coagulation." Jour. Amer. Water Works Assoc., 54, 971 (1962).
- 29. Weber, W. J., Jr., <u>Physicochemical Processes for Water Quality</u> Control, Wiley-Interscience, New York, N.Y. (1972).
- 30. <u>Handbook of Chemistry and Physics</u>, 51st Ed., Chemical Rubber Company, Cleveland, Ohio (1970).
- 31. Camp, T.R., "Hydraulics of Mixing Tanks." Jour. Boston Soc. of Civil Engr., 56, 1 (1969).
- 32. Camp, T.R., and Stein, P.C., "Velocity Gradients and Internal Work in Fluid Motion." Jour. Boston Soc. of Civil Engr., 30, 219 (1943).
- 33. Camp, T.R., "Flocculation and Flocculation Basins." <u>Trans.</u> <u>Amer. Soc. Civil Engr.</u>, 120, 1 (1955).
- Edzwald, J.K., et al., "Coagulation in Estuaries," <u>Environ. Sci.</u> <u>& Technol.</u>, 8, 58 (1974).
- TeKippe, R.J., and Ham, R.K., "Coagulation Testing A Comparison of Techniques." Jour. Amer. Water Works Assoc., 62, 620 (1970).
- 36. Stamberg, J.B., et al., "Lime Precipitation in Municipal Wastewaters." U.S. Dept. of Interior, Federal Water Pollution Control Administration, Advanced Wastewater Treatment Research Laboratory (1969).
- Packham, R.F., "The Coagulation Process A Review of Some Recent Investigations." <u>Proc. of the Soc. for Water Treat. and</u> <u>Examin.</u>, 12, 84 (1963).
- 38. Recht, H.L., and Ghassemi, M., "Kinetics and Mechanism of Precipitation and Nature of the Precipitate Obtained in Phosphate Removal from Wastewater Using Aluminum (III) and Iron (III) Salts." Environmental Protection Agency Program No. 17010 EKI, Cincinnati, Obio (1970).

- Department of Public Utilities, Gainesville, Florida, "Magnesium Carbonate, a Recycled Coagulant for Water Treatment, "Environmental Protection Agency Project No. 12120 ESW, Washington, D.C. (1971).
- 40. Ghassemi, M., and Recht, H.L., "Phosphate Precipitation with Ferrous Lime." Environmental Protection Agency Project No. 17010 EKI, Washington, D.C. (1971).
- Ketchum, L.H., Jr., and Weber, W.J., Jr., "Coagulation of Stormwaters and Low Alkalinity Wastewaters." Jour. Water Poll. Control Fed., 46, 53 (1974).
- 42. Metcalf & Eddy, Inc., Wastewater Engineering, McGraw-Hill Book Co., New York, N.Y. (1972).
- 43. Jankovic, S.G., et al., "Measurement of Phosphorus in Wastewater." Water and Sew. Works, 114, 471 (1967).
- 44. Standard Methods for the Examination of Water and Wastewater, 13th Ed., Amer. Public Health Assoc., New York, N.Y. (1971).
- Ferguson, J.F., et al., "Calcium Phosphate Precipitation at Slightly Alkaline pH Values," Jour. Water Poll. Control Fed., <u>45</u>, 620 (1973).
- 46. Black & Veatch, Consulting Engineers, <u>Process Design Manual for</u> <u>Phosphorus Removal</u>, Environmental Protection Agency, Program No. 17010 GNP (1971).
- 47. Walker, J.D., "High Energy Flocculation and Air-and-Water Backwashing," Jour. Amer. Water Works Assoc., 60, 321 (1968).
- 48. Camp, T.R., "Sedimentation and the Design of Settling Tanks." Trans. Amer. Soc. of Civil Engr., 111, 895 (1946).
- 49. Eckenfelder, W. W., and O'Connor, D. J., <u>Biological Waste Treat-</u> ment, Pergamon Press, New York, N.Y. (1961).
- 50. Nebiker, J.H., et al., "An Investigation of Sludge Dewatering Rates." Jour. Water Poll. Control Fed., 41, R255 (1969).
- 51. Adrian, D. D., and Smith, J. E., Jr., "Dewatering of Physical-Chemical Sludges." Conf. on Applications of New Concepts of Physical-Chemical Wastewater Treatment, Vanderbilt University, Nashville, Tennessee (1972).

DEPARTMENT OF COMMUNICATION STUDIES GRADUATE PROGRAM HANDBOOK

1975-76

UNIVERSITY OF MASSACHUSETTS/Amherst

RECEIVED

.

.

OCT 3 0 19/5

MASS. DIVISION OF WATER POLLUTION CONTROL WESTBORD OFFICE